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ON THE DETERMINATION OF PHOSPHORIC ACID AS MAGNESIUM PYROPHOSPHATE.[1]

BY HUGO NEUBAUER.

TRANSLATED AND ABSTRACTED BY K. P. MCELROY.

AFTER giving a brief history of the molybdenum method for the determination of phosphoric acid, Herr Neubauer states his reasons for thinking this method undeserving of its high repute for accuracy. He next gives the results of a long investigation of the sources of error inherent in the method.

As a standard silver orthophosphate was employed, this salt being chosen partly because of its perfectly definite composition, partly because of the ease with which the base could be estimated. Magnesium ammonium phosphate was rejected for this purpose because it was not thought proper to have the same salt serve as both the beginning and the end. Disodium phosphate was rejected because, of its tendency to absorb carbonic acid. In the first series of experiments on the molybdate method (Wagner's modification), the amount of phosphoric acid found was a trifle less than that known to have been used, the discrepancy ranging from 0.3 mgm. on 84.2 mgms. P_2O_5 to 2.7 mgms. on 166.8 mgms. P_2O_5. Two explanations could be made of this loss—either that the precipitations were not complete or that volatilization of the phosphoric acid occurred during the ignition of the magnesium salt previous to weighing. Neubauer rejected the former explanation in favor of the latter, adducing a series of

[1] Presented to the World's Chemical Congress, Chicago, August 22, 1893.

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experiments in favor of his view. The lid of a platinum crucible was covered with a layer of magnesium hydroxide on the under side and ignited till magnesium oxide was formed and the weight of the lid remained constant. A filter containing magnesium phosphate was then burned in the crucible and after the combustion of the paper, the lid was placed in position and the salt ignited to constant weight. The lid was found to have increased in weight in amounts varying from 0.2 mgm. to 3.8 mgms. The smaller amount was found where the phosphoric acid was directly precipitated and also in a case where magnesium ammonium phosphate reputed to be chemically pure was directly ignited. The largest increase in weight was found in cases where large quantities (five grams) of ammonium chloride or molybdate were added previous to the precipitation of the double phosphate. In the precipitate obtained by the Wagner process (in this method the ammoniacal solution of the yellow precipitate is not neutralized previous to adding the magnesia mixture) the increase varied from 0.5 mgm. to 2.0 mgms. On solution of the magnesia layer on the lid, phosphoric acid was detected by the molybdate reaction. The observation is made that precipitates exposed to the heat of a common Bunsen burner are but little below the truth, while the weights of large precipitates obtained by the molybdate method are often several milligrams too low after strong ignition. The argument is made that the molybdic acid cannot be responsible for this peculiar behavior, since the precipitate when washed till the chlorine reaction disappears contains but an insignificant amount of this substance. Magnesium ammonium phosphate covered before ignition with a weighed amount of lime or magnesia, weighs more than a similar precipitate ignited without this addition, in case an excess of ammonium salts has been present during the precipitation. If the washed precipitate of magnesium ammonium phosphate is dissolved in a very little hydrochloric acid, ammonia in excess added and then two cc. of magnesia mixture, the double precipitated salt will weigh more than it would have done otherwise in case much ammonium molybdate was originally present.

From these facts the conclusion is drawn that in the presence of an excess of ammonium salts, the magnesian precipitate is not

pure dimagnesium ammonium phosphate ($MgNH_4PO_4$), but contains more or less monomagnesium ammonium phosphate ($Mg(NH_4)_4(PO_4)_2$). This latter salt decomposes on ignition into magnesium metaphosphate, ammonia, and water. On further ignition, this phosphate becomes converted into pyrophosphate, and phosphorus pentoxide is set free and volatilized.

$$Mg(NH_4)_4(PO_4)_2 = Mg(PO_3)_2 + 4NH_3 + 2H_2O.$$

$$2Mg(PO_3)_2 = Mg_2P_2O_7 + P_2O_5.$$

The greater the concentration of the ammonium salts, the larger the amount of monomagnesium salt which will be formed. For this reason the prevailing ideas relative to the concentration of the solutions to be precipitated are erroneous and more accurate results can be obtained by greater dilution.

Two chances of error exist in the determination of phosphoric acid by the magnesian method—first, that the precipitate may contain too much magnesia, second, that it may contain too little. The second error is readily detected by the method already given. The other may be detected by Tollen's method (*J. Landw*, *1882*, **30,** 48), which consists in suspending the ignited phosphate in water, adding a little dilute solution of silver nitrate and heating. In the presence of an excess of magnesium, silver orthophosphate is formed and recognized by its yellow color. The reaction is sufficiently sensitive.

Experiments were made with solution of pure magnesium ammonium phosphate containing various amounts of ammonium chloride. In one solution containing 300 mgms. of the chloride, half a milligram of magnesia was found in the filtrate after precipitation by ammonia, and the same quantity of phosphorus pentoxide was volatilized on ignition of the precipitate. In another case where 2.5 grams of ammonium chloride were present, the loss in magnesia and phosphoric oxide were respectively 1.1 and 1.6 mgms. In a third where five grams were employed, the losses were 3.2 and 4.4 mgms. respectively. Finally, phosphoric acid (44.8 mgms.) was precipitated in the presence of 200 cc. of approximately saturated solution of ammonium chloride. The losses reached the large figures of 12.7 and 15.6 mgms. respectively for MgO and P_2O_5. The filtrate contained phosphoric acid in amount sufficient to permit its recognition by molybdate, but there was not enough to determine.

Even in the absence of an excess of magnesium chloride the phosphoric acid is wholly precipitated, although ammonium chloride may be present in large amount. The precipitate thus obtained is, however, never of the correct composition. It invariably contains an excess of phosphoric acid and this excess is proportional to the amount of sal ammoniac present. This error is not counteracted by the presence of an amount of magnesium chloride sufficient to form a precipitate of the proper composition.

In the presence of an excess of magnesium chloride the precipitate invariably contains at least enough magnesia to form the normal salt, even in the presence of an excess of ammonium salts. A pure precipitate is, however, only obtained when the amount of free ammonia present is just sufficient for its formation. Any excess of the base causes the precipitate to contain too much magnesia. When ammonia is allowed to slowly flow into a solution containing phosphoric acid and a magnesium salt in excess, the precipitate formed has the normal composition, provided that the rate of flow has been so regulated that the precipitation has taken place in neutral solution. Of course an excess of ammonia must be finally added in order to secure complete precipitation, but this excess is not injurious after the precipitate has once formed.

Various attempts were made to secure a process giving reliable results and yet not too clumsy for practice. Ammoniacal solution of phosphomolybdic acid was neutralized with hydrochloric acid till the yellow precipitate no longer disappeared on stirring and no smell of ammonia could be detected, neutral magnesium chloride solution containing ammonium chloride added, and then dilute ammonia, till a precipitate began to appear. The solution was allowed to stand for awhile, a trifle more ammonia added, and finally, after another wait, an excess of ammonia. By this process correct results were occasionally obtained, but usually the precipitate was a trifle (0.0 to 1.5 mgms.) too heavy and gave Tollen's reaction. For many purposes the results are sufficiently close.

It is probable that in the presence of excess of magnesium chloride and of ammonia some trimagnesium phosphate is

formed, for it is not likely that the excess of magnesia in the precipitate is due to oxide mechanically carried down in the precipitate when quickly formed.

When hydrochloric acid is added to an ammoniacal solution of phosphomolybdate till the precipitate redissolves with difficulty on stirring, the solution reddens blue litmus paper and probably contains free phosphomolybdic acid. On now adding first magnesium chloride in excess and then ammonia, ammonium phosphomolybdate is probably first formed, and then this salt gradually breaks up as more ammonia is added, forming magnesium ammonium phosphate with the magnesia already in solution.

Precipitates obtained from solutions approximately neutral often contain noticeable proportions of molybdic acid in the free state. This is caused by the decomposition of phosphomolybdic acid by ammonia and magnesium chloride. As molybdic acid is not particularly soluble in water, it is deposited simultaneously with the magnesium ammonium phosphate and is enclosed by the latter salt to some extent, and so shielded from the solvent action of the excess of ammonia later added. This separation of free molybdic acid, of course, does not occur in the presence of free ammonia.

The difficulty of preparing the pure double phosphate is not so great in the absence of molybdate and when the excess of magnesium chloride is not large. Washed magnesian precipitates dissolved in hydrochloric acid containing a slight amount of magnesium chloride, and carefully reprecipitated with ammonia, gave better results than had been hitherto obtained. The process is, however, too dependent on the skill of the operator to be reliable.

Magnesium ammonium phosphate can be obtained in three different conditions:

(1) The precipitate is formed in neutral or ammoniacal solution containing no excess of magnesium salt. The result of this is that the precipitate contains less than the normal amount of magnesia, and phosphoric oxide is volatilized on ignition. Therefore weights come out too low.

(2) The precipitate is formed in the presence of an excess of

magnesium salt, but during its formation ammonia is not present in excess. As a result the precipitate possesses the normal constitution and the weights obtained are correct.

(3) The precipitate is formed in the presence of an excess of both ammonia and magnesium salts. The result is that the precipitate contains an excess of magnesia and the weights afforded are consequently too high.

Viewing in the light of these results the method for the precipitation of phosphoric acid (that of Abesser, Jani and Maercker), in which the ammoniacal solution of the yellow precipitate is approximately neutralized with hydrochloric acid, magnesia mixture then added, and subsequently an excess of ammonia, it is readily seen that the following sources of error exist:

A. The whole precipitate is formed as is indicated under (1). This occurs when the amount of ammonia present in the magnesia mixture is so large that precipitation of the phosphoric acid is at once effected when the reagent is slowly added and the liquid stirred, excess of magnesia not being present during the precipitation. Subsequent addition of excess of magnesium chloride or of ammonia is of no avail. The results are similar to those obtained by Wagner's process (in which the neutralization with hydrochloric acid is not practiced).

B. In the formation of the precipitate all three conditions successively occur. This is the case when the amount of ammonia in the magnesia mixture is such that when the reagent is added, drop by drop, stirring constantly, precipitation begins while there is no excess of magnesia, but continues after an excess has been added. Under these circumstances the errors may nearly balance. It is not practicable to form the precipitate wholly of the composition given under (2).

C. When magnesia mixture and ammonia are added drop by drop, stirring constantly, the precipitate formed generally has the composition given under (2) and (3). The 2.5 per cent. ammonia of the usual magnesia mixture is so weak that the precipitate begins to form when magnesia is in excess. The results are consequently too high, and the quicker the precipitation has been effected the higher the results are likely to be, from the

fact that a smaller portion of the precipitate is formed in neutral solution.

D. The precipitate is exclusively of the composition given under (3) only when magnesia mixture and ammonia are too quickly added. The results are in this case even higher than those just referred to under C.

These theoretical conclusions were confirmed by direct experiment.

The common citrate method gives approximate results which is due to the fact that two sources of error counterbalance each other. On the one hand the precipitate invariably contains lime and on the other the phosphoric acid is not completely precipitated. When magnesia mixture is slowly added to an ammoniacal solution of phosphoric acid containing ammonium citrate but no bases forming insoluble salts with phosphoric acid, the precipitate forms mostly in the condition given under (1) and but little in that given under (3), inasmuch as most of it is formed in the absence of an excess of magnesium chloride. This view was confirmed by experiment, but it was also shown that even when the magnesia was rapidly added, some phosphoric acid was volatilized during the subsequent ignition of the precipitate. This is due to the fact that from solutions of phosphoric acid containing no lime salts the precipitate is formed with tolerable rapidity even where citrate was present, so that on the addition of the magnesia mixture a portion of the precipitate is formed in the absence of an excess of magnesium chloride.

The general conclusion drawn from the results of a number of determinations made by various modifications of the molybdate method and by the citrate method is that none of these methods is particularly accurate. It appears practically impossible to completely convert phosphoric acid into pure magnesium pyrophosphate under analytical conditions, where the molybdate method is employed. The exact amount of phosphoric acid in a substance can therefore only be obtained by correcting the results analytically found by a factor, assuming that the errors of analysis are constant for a given amount of phosphoric acid.

Results obtained, where the neutralization with hydrochloric acid is practiced, are oftener nearer the truth than where this

precaution is omitted. However, results thus obtained are dependent on so many sources of error that it is difficult to make parallel analyses. Besides this the method is rather inconvenient. The molybdic acid occurring in the precipitate is a nuisance. Its complete removal by ignition requires skill and practice, and often as much time as the expulsion of the volatile phosphoric acid from the precipitate formed where neutralization is omitted (Wagner's modification). On the other hand the latter modification of the method is very convenient in practice and the attendant relations are so simple, that duplicates must agree where simple precautions are observed.

A systematic determination was made of the errors attendant on Wagner's method and from the results a table constructed, the use of which is recommended for phosphate determinations. The source of error in this method lies exclusively in the loss of phosphoric acid by volatilization. The magnesia-covered crucible lid offers a very good control of this error and its use is recommended to the analyst. Of course, the presence of sulphur in the gas used for ignition is liable to disturb this check.

The following course of procedure in the determination of phosphoric acid can be recommended:

Separate the phosphoric acid in the form of the yellow precipitate and wash this latter in the usual way. Too high a heat should not be employed, nor should the solutions be allowed to stand too long lest excess of molybdic acid separate. Dissolve the phosphomolybdate in 100 cc. of cold 2.5 per cent. ammonia and add as many cc. of the usual magnesia mixture (fifty-five grams magnesium chloride and seventy grams ammonium chloride dissolved in a liter of 2.5 per cent. ammonia) as there are centigrams of phosphoric acid present. Addition should not be made faster than ten cc. per minute. Stir during the addition. After the precipitation stir briskly once more and then allow to stand at least three hours. Wash with 2.5 per cent. ammonia till the chlorine reaction disappears, dry the filter and introduce into a well-cleaned crucible which has been thoroughly ignited. Place the lid at an angle, carbonize the filter and gradually raise the heat, though not higher than a medium red heat, till the pyrophosphate becomes completely white. When

this happens bring the blast into action and ignite to constant weight. The weight finally accepted must not change even after half an hour's ignition. Upon this requirement especial stress must be laid. Pure magnesium pyrophosphate does not suffer any loss even after several hours' ignition, nor does a good platinum crucible. To the weighed amount of pyrophosphate add the correction given in the table. Multiplication of the sum by 64 gives the amount of phosphoric acid in the weight taken for analysis.

CORRECTION FOR PHOSPHORIC ACID DETERMINATION.

Found, $Mg_2P_2O_7$ in grams.	Lost, milligrams $Mg_2P_2O_7$.	Found, $Mg_2P_2O_7$ in grams.	Lost, milligrams $Mg_2P_2O_7$.
0.10	0.6	0.24	4.0
0.12	0.8	0.25	4.2
0.14	1.2	0.26	4.6
0.15	1.4	0.27	5.0
0.16	1.6	0.28	5.5
0.17	2.4	0.29	6.1
0.18	2.6	0.30	6.8
0.19	3.2	0.31	7.6
0.20	3.5	0.32	8.6
0.21	3.6	0.33	9.6
0.22	3.8	0.34	10.6

When phosphoric acid is to be estimated as pyrophosphate it must always be first separated as molybdate, even when the original solution contained no bases capable of forming insoluble phosphates, as otherwise these corrections will not be applicable.

Using these corrections, the estimation of phosphoric acid becomes one of the most accurate of known analytical methods.

EXPERIMENTS ON A FERRO-TUNGSTEN.

BY JAMES S. DE BENNEVILLE.

Received February 28, 1894.

IN making an analysis of a ferro-tungsten rich in tungsten the chemical behavior of a residue insoluble in acids and apparently not decomposed by fused solvents led me to believe that it was metallic tungsten. The time available was limited and the few experiments made were hasty and at intervals, and in a private communication describing the method pursued in analy-

sis I called attention to the insufficient basis on which the analysis rested and the necessity for further investigation. The work involved in this paper was undertaken to determine, if possible, whether tungsten existed uncombined in the alloy and whether any definite ratio between tungsten and iron could be shown or alloys separated. The results showed that what was taken to be tungsten was a rich tungsten alloy the iron of which was not attacked by acids and which in its indifference toward chemical reagents resembled metallic tungsten.

The method of analysis adopted was directed toward determining how different solvents would act on the alloy. The steps taken were from the less to the more energetic reagent and consisted in 1. Attack by strong hydrochloric acid and determination of the iron and tungsten so removed in solution. 2. Fusion of the residue with a mixture of alkali carbonate and nitrate. 3. Action of solution of silver nitrate on the alloy.

The results based on sixteen analyses showed the alloy to be very heterogeneous. The sample was in the form of small fragments showing to the eye the differentiation throughout the mass and even the fragments themselves had not the same appearance, some of them having a number of cleavage planes of a pyritous appearance. In making these later analyses no effort was made to obtain a uniform sample, but the contrary, for the object sought was to ascertain whether all the iron was alloyed with tungsten or *vice versa;* and whether iron and tungsten were present as such dissolved in a true alloy.

A marked regularity was shown in the amount of tungsten dissolved on treating the alloy with ammoniacal silver nitrate solution. However, on digesting with neutral solution of silver nitrate no tungstic acid separated and the silver precipitated was in proportion to the iron dissolved. This absence of tungstic acid from the residue pointed to the fact that all the tungsten was in the form of alloy. The small quantity of iron separated did not calculate to any definite ratio with the tungsten acted on by the silver salt. Part of the iron was probably due to the steel mortar in which, owing to its great hardness, it was necessary to crush the alloy. This would vitiate any calculation.

The results, under I, were obtained by the following method: The fragments of the alloy were powdered separately in a steel mortar and passed through a sixty mesh sieve. Weighed portions were then extracted by strong hydrochloric acid (sp. gr. 1.20) until the acid no longer acted. In this solution iron and tungsten were determined. The residue was fused with a mixture of sodium carbonate and nitrate and the fusion lixiviated in water. Decomposition was complete. Iron and tungsten were determined. The results obtained were as follows:

I. To One Gram.

No.	1	2	3	4
Acid extract, iron	0.3648	0.3779	0.3631	0.3853
Acid extract, tungsten..	0.0233	0.0309	0.0217	0.0282
Residue, iron.....	0.1786	0.1762	0.1669	0.1416
Residue, tungsten.....	0.4333	0.4057	0.4390	0.4626

Taken in connection with II this table appears to show that part of the alloy is readily attacked by acid, iron being dissolved and the tungsten left behind in the residue. This is indicated by the small quantity of free iron (see II) in the majority of the samples taken for analysis. Any large quantity of unalloyed iron would be shown very positively. This does not show necessarily the separation of an easily decomposed alloy from others less readily attacked. Other facts, given later, indicate that this alloy is an unsaturated compound and that a still higher percentage of tungsten than given in these analyses can be held chemically combined with the iron, but the higher valency exercised by the iron in these rich tungsten compounds may not be the most stable.

It was sought to ascertain how the alloy would act toward silver solution. Four reactions were involved. 1. Metallic iron, reducing silver from its salts in the ratio of Fe:2Ag. The reaction takes place in neutral solution. 2. Metallic tungsten and silver salt in neutral solution. 3. Metallic tungsten and silver salt in ammoniacal solution. 4. Action of the tungsten in this alloy on the silver salt. In the neutral solution of silver nitrate tungsten is converted into tungstic acid and silver is reduced. Silver tungstate is also formed. After washing the precipitated tungstic acid and silver free from excess of silver nitrate and dissolving in ammonia the black silver sulphide was obtained by

ammonium sulphide. The quantity was small but this salt is somewhat soluble in water[1] and washing must have removed some portion of it. The main bulk of the flocculent white precipitate is tungstic acid. In the ammoniacal solution of silver nitrate the tungstic acid formed dissolves leaving silver as residue.

The results obtained from experiments carried out on this line indicated the amount of free iron and by dissolving it out left the residue ready for further treatment. The alloyed ferro-tungsten did not appear to be attacked by the silver nitrate, which was to be expected from the strong affinity of iron for tungsten. In two analyses, however (18 and 19), in which a large quantity of iron replacing silver was found, the tungsten instead of dropping to a low percentage remained near the average found in nearly all the analyses, forty per cent. This looks as if the alloyed ferro-tungsten had been attacked by the reagent, but it can be explained on the ground of segregation. Crookes[2] in criticising Schöffel's method for chrome and tungsten steels by solution of the iron in copper ammonium chloride notes the fact that steels containing a high percentage of chromium (eight per cent.) or tungsten (twelve per cent.) are but slightly attacked.

To make use of the reaction that in ammoniacal solution of silver nitrate tungsten replaces silver in the ratio of W : 6Ag the following analytical method was adopted:

Weighed portions of the alloy were digested for thirty hours with a neutral solution of silver nitrate. This solution was decanted from the heavy residue and washed by decantation with water. After removal of the excess of silver, iron was determined in this solution giving the quantity of free iron. It was noticeable that in nearly all the analyses this was very small and in part was due probably to fragments from the mortar. In two of the analyses this "free iron" is a considerable percentage of the whole and cannot be put down to that cause. After removal of the neutral silver salt the residue was digested for from thirty-six hours to a week with an excess of ammoniacal solution of silver nitrate. This solution was filtered and the residue

[1] E. F. Smith and Bradbury, *J. Anal. Appl. Chem.*, 5, 486.
[2] Crookes "Select Chemical Methods," pp. 217–219.

washed with water. Silver was removed from the ammoniacal solution by ammonium sulphide and tungsten determined in the filtrate. The residue from the treatment with the silver salt was dried and ignited. Silver was removed by nitric acid and the final residue obtained was fused with a mixture of sodium carbonate and saltpeter. Tungsten was precipitated from the neutral solution of alkali tungstate as mercurous salt. Iron was determined where found. This method of analysis separated the constituents into 1. Iron replacing silver. 2. Tungsten replacing silver. 3. Unattacked iron and tungsten.

The experimental results tabulated were:

III. 9–12 with neutral solution of silver salt; 13–15 with ammoniacal solution of silver salt; 16–20 with neutral and subsequently ammoniacal solution of silver salt.

III. CALCULATED TO ONE GRAM. ALLOY TREATED WITH SILVER SALT.

No.	Total iron. A.	Total tungsten. B.	"Free" iron. C.	"Free" tungsten. D.	Residual iron. E.	Residual tungsten. F.	A : B less "free" iron ratio. G.
9....	0.4068	0.5758	0.0070	....	0.3998	....	7:3
10....	0.4698	0.5081	0.0150	....	0.4548	....	3:1
11....	0.5919	0.3889	0.0072	....	0.5847	....	5:1
12....	0.5199	0.4552	....	0.0453	....	0.4099	..
13....	0.6861	0.2986	....	0.0586	....	0.2400	..
14....	0.6207	0.3700	....	0.0692	....	0.3008	..
15....	0.5118	0.4789	0.0121	0.0399	0.4997	0.4390	0.7:2
16....	0.4075	0.5842	0.0281	0.0522	0.3794	0.5320	0.2:1
17....	0.5227	0.4680	0.0561	0.0367	0.4666	0.4313	3.26:1
18....	0.5221	0.4686	0.3147	0.0626	0.2074	0.4060	3:2
19....	0.4847	0.4933	0.3430	0.0535	0.1444	0.4398	1:1
20....	0.5178	0.4689	0.0150	0.0534	0.5028	0.4155	7:2

The term "free" iron and "free" tungsten is used to indicate the quantity of those metals replacing silver in the silver solution.

The variation in the analytical results appears to show that we have to deal with a number of alloys and these not distributed evenly through the mass. The small quantity of iron replacing silver in silver nitrate indicates that the iron is in combination with the tungsten and not a number of more or less complex alloys dissolved in a matrix of metallic iron. Nos. 18 and 19 can be attributed to segregation on cooling, such segregation taking place when the mass was not very liquid in which case

the separated and unalloyed iron would surround a rich tungsten alloy. Schneider[1] separated from a high tungsten iron what appeared to be two alloys corresponding to the formulas Fe_3W and Fe_6W. If iron be regarded as divalent the saturation point of tungsten would be reached in the formula Fe_3W (taking tungsten as hexavalent). If iron be regarded as octovalent the saturation formula would be Fe_3W_4. Howe in his "Metallurgy of Steel" states that "tungsten unites with iron apparently in all proportions at least up to eighty per cent." The following table of analyses is taken from his work quoted, p. 81:

No.	1.	2.	3.	4.	5.	6.
Tungsten.....	37	77.8	53.1	29.12	24.25	28.18
Iron.....	63	16.4	43.4	67.93	30.	68.36
Manganese....	..	5.8	3.5	but little	41.50	0.99
Silicon	..	....	....	0.61	....	0.23
Carbon	..	....	....	1.17	5.65	1.88
Phosphorus ...	..	....	....	....	0.14	0.008

The description given of No. 3, "platinum gray, hard, brittle, lamellar completely fusible" would in the first three qualities apply directly to the ferro-tungsten under consideration. Analysis No. 2 very closely approximates the formula Fe_3W_4 and if no alloy of iron and tungsten, in combination, containing a higher percentage of tungsten, exists, it would point strongly to the octovalency of iron in its combinations with this element as metal. The other analyses, including those of the ferro-tungsten under consideration would be unsaturated compounds. This valency has been shown to belong to other members of this family. Ruthenium and osmium in their oxides, iron in ferric acid, appear as hexavalent and the existence of the ammonia cobalt salts indicate a still higher valency for a metal closely allied to iron.[2]

Mendelejeff compares alloys to solutions as indefinite unstable compounds. In solutions in which there is free communication within the bounds of the liquid on alteration in temperature a change in molecular composition occurs as is shown by the separation of definite salts limited by such temperature. An alloy in the fused state is then analogous to a solution and when during

[1] Howe's Metallurgy of Steel, p. 81.

[2] Lothar Meyer, "Modern Theories of Chemistry," pp. 347, 348.

cooling segregation sets in the different alloys crystallize out from the mass. If the iron were present in such quantity that its saturation capacity for the tungsten would drop below divalency metallic iron would appear in this alloy but this is not the case.

The fact that iron does not replace silver in the silver nitrate or copper in the copper ammonium chloride shows a very strong affinity of iron for tungsten. If the bond between the iron and tungsten atoms was weak, or if there was merely a mechanical mixture, iron should replace silver in the neutral solution of the silver salt. This is based on the fact that "a positive element is separated from its combinations with a negative element by a stronger positive," and iron is more positive than silver.[1] Iron and tungsten are so separated in their properties as metal and semi-metal that an alloy of such constituents should be a very stable compound.

Metallic tungsten is left almost unattacked by hot acid. The action of aqua regia slowly converts it into tungstic acid. The acid must be used in small portions at a time and adhering tungstic acid removed by ammonia to prevent its protective action. Fusion with potassium bisulphate, or with caustic soda, or alkaline carbonate and saltpeter decomposes it.

In its action toward acids the alloy shows very strongly the influence of the tungsten. Acids do not act on it energetically as with carbon steel. To a degree this is to be expected but its inertness is almost as marked as with metallic tungsten. Hydrochloric acid dissolves out about two-thirds of the iron and a little tungsten. Nitric acid does the same. Part of the alloyed iron, therefore, appears to be attacked by acid solvents. Sulphuric acid barely acts upon it but fusion with potassium bisulphate (sulphuric acid at a red heat) decomposes the alloy completely. Aqua regia attacks it slowly but action is soon stopped by the tungstic acid forming a coating which must be removed to obtain further action on the alloy by the solvent. This chemical behavior points to a complex molecular structure. The formula Fe_3W_4 is purely empirical and the true formula is probably a very large multiple of this. If the fusibility and volatility of

[1] Modern Theories of Chemistry, pp. 515-517.

compounds diminishes with increasing complexity of structure then in such difficultly volatile metals as tungsten, chromium, platinum, and other metals fusing at high temperatures, and in their alloys, the molecule (in the solid state) must be possessed of large molecular weight and corresponding inertness toward chemical action.[1]

I am indebted to Dr. Wahl, of Philadelphia, through Mr. Garrison, for the material on which these analyses were made.

THE DIRECT ESTIMATION OF CITRATE SOLUBLE PHOSPHORIC ACID.

By B. B. Ross.

Received December 18, 1893.

THE direct determination of citrate soluble phosphoric acid, as is well known, is effected in many European laboratories by precipitating it, as magnesium ammonium phosphate in the presence of the ammonium citrate employed in effecting its solution.

The lack of general applicability, together with other objections, which have been urged against this method, however, has caused its employment to be somewhat restricted and the process has met with little favor in this country.

The presence of the citric acid in the solution has, of course, prevented the direct application of the molybdate method, and several processes have been proposed for the elimination of the citric acid preparatory to the precipitation of the phosphoric acid by the molybdate solution. The writer some years since (Proceedings Association Official Agricultural Chemists, 1885,) proposed the removal of the citric acid by precipitation in the hot solution by means of calcium chloride.

A number of results reported at that time showed quite a close agreement with the figures obtained by the regular official method, but some later tests indicated a loss resulting from the retention of small quantities of calcium phosphate in the precipitate of calcium citrate.

[1] "Modern Theories of Chemistry," pp. 131, 287. Ostwald "Outlines of General Chemistry," pp. 190, 191; in reference to potassium as solid p. 275.

Kuntze (*Ztschr. f. Rübenzucker, 1892*, 860,) recommends for the destruction of citric acid and other organic matters, evaporation of the solution and treatment with sulphuric and nitric acids, followed by thorough ignition. During the past year a number of experiments were made in the laboratory of the Louisiana State University with a view to the elimination of citric acid by means of oxidizing agents by the wet way.

After testing a number of different methods of oxidation it was found that the best and most satisfactory results were to be secured by the employment of the Kjeldahl digestion process. The mode of procedure finally adopted is essentially as follows:

After the completion of the thirty minutes' digestion of the sample with 100 cc. of citrate solution, twenty-five cc. of the liquid are at once filtered out into a dry vessel, preferably into a burette, as the solution can, after cooling, be transferred to another vessel without the dilution attendant upon rinsing the measuring vessel.

Bring the aliquot, thus measured, into a digestion flask of 250 to 300 cc. capacity, add about fifteen cc. concentrated sulphuric acid and place the flask on a piece of gauze over a moderately brisk flame.

Within about eight minutes the liquid will have become quite concentrated and will begin to darken appreciably and at the same time foaming will commence, but will occasion no trouble if an extremely high, or a very low flame be avoided.

After a further lapse of three or four minutes the foaming ceases and the contents of the flask appear quite black; about one gram of mercuric oxide or metallic mercury is now added and the digestion continued over a high flame.

The operation can be readily completed within less than half an hour, and, in many cases, within twenty-five minutes, a clear and almost colorless liquid being obtained.

After cooling, the solution is washed into a beaker, ammonia is added in slight excess, the solution acidified with nitric acid and the regular molybdate method followed, after addition of ammonium nitrate.

In case as large an amount as fifty cc. (corresponding to one gram of the sample) of the filtrate from the citrate treatment is

employed, ten cc. of strong sulphuric acid are at first added and the digestion conducted in a flask of 350 to 500 cc. capacity; after the contents of the flask have blackened and the foaming has progressed considerably, the flask is removed from the flame and fifteen cc. more of sulphuric acid are added and the flask and contents heated with a low flame for two or three minutes; mercuric oxide is next added and the digestion is completed as before described.

Among the chief advantages of this process for the determination of citrate soluble phosphoric acid may be enumerated the following:

1st.—It affords a quick and direct method for the estimation of that form of phosphoric acid which, together with the water soluble, constitutes what is termed "available" phosphoric acid, and the amount of this available phosphoric acid is thus reached by two determinations instead of three according to the ordinary method.

2nd.—The economy of time and labor attendant upon this process gives it an advantage over the indirect method, since by the direct method it is only necessary to filter out twenty-five cc. (or possibly fifty cc.) of the citrate solution, thus obviating the frequently tedious task of filtering the whole liquid and bringing upon the filter and washing with water of a definite temperature the insoluble residue; in addition, the ignition of this residue, the subsequent digestion with acid, dilution to a definite volume and measurement of an aliquot, are operations which are either tedious or time-consuming and can to a large extent be avoided by the use of the direct process.

3rd.—If it is desired, this method can be used as a check or control process in connection with the regular method, the check determination being readily executed without the necessity of weighing a fresh quantity of the sample under examination.

The results of a number of comparative tests of this process and the regular official method are herewith inserted, the principal portions of the work reported having been performed by Mr. R. E. Blouin, assistant chemist, during the past fertilizer season.

The samples tested were ordinary commercial fertilizers and

it will be observed that the agreement in the figures obtained by the two processes is, in the main, quite close.

RESULTS OF CITRATE-SOLUBLE DETERMINATIONS.

		By the direct method.	By difference, (Official method).
Sample No.	1	2.16	2.16
" "	2	5.63	5.67
" "	3	5.37	5.39
" "	4	2.44	2.64
" "	5	2.00	1.86
" "	6	5.40	5.33
" "	7	6.90	6.78
" "	8	4.55	4.51
" "	9	2.75	2.73
" "	10	2.04	1.98
" "	11	2.07	2.09
" "	12	6.46	6.48
" "	13	5.24	5.11
" "	14	5.12	5.06
" "	15	2.87	2.91
" "	16	1.61	1.53
" "	17	0.37	0.33
" "	18	0.94	0.90
" "	19	0.33	0.36

In order to further test the reliability of the method, a solution containing phosphoric acid derived from a chemically pure phosphate was employed and phosphoric acid in the aqueous solution was determined by the regular molybdate method; a given quantity of the same solution was next mixed with twenty-five cc. of ammonium citrate solution and after addition of fifteen cc. sulphuric acid, the digestion was conducted as before described and the phosphoric acid determined in the manner previously stated. The results were:

By first method (direct molybdate process) 8.06 per cent.
By second method (addition of citrate solution, etc.) 8.13 per cent.

Other tests with chemically pure salts showed differences which were well within the limits of variation permissible in ordinary analytical work.

Experiments were also made with employment of potassium nitrate in the place of mercuric oxide, but it was found that a number of additions of this substance was required and the time

needed for the completion of the digestion was considerably lengthened.

The Gunning modification of the Kjeldahl digestion process was also tested but the foaming resulting from the employment of the large quantities of potassium sulphate rendered the use of this modification impracticable.

By the employment of either mercuric oxide or metallic mercury, however, the oxidation is effected rapidly and completely and the subsequent precipitation of the phosphoric acid is easily accomplished.

NOTES ON THE ESTIMATION OF CRUDE FIBER IN SUGAR CANE.

By J. L. Beeson, Ph.D., Professor of Chemistry, Louisiana Sugar School, New Orleans.

Received February 26, 1894.

THERE is no part of the analytical work connected with the chemical control of diffusion process sugar house so unsatisfactory as that of the estimation of the so-called "crude fiber" in the cane, or that portion of the stalk which is insoluble in water. Duplicate analyses, manipulated with great care, show wide variations. The average of such variations for 100 samples taken consecutively was 0.736 per cent. Since the percentage of fiber is used as a factor in calculating the percentage of sucrose on the weight of the cane it becomes highly desirable that either a better method of fiber estimation be devised, or a more accurate and quick method of estimating the percentage of the sucrose directly on the weight of the cane. After a systematic and thorough investigation of the subject I have come to the conclusion that a very accurate method of fiber estimation for technical purposes is not feasible, on account of the wide variation in fiber content in different parts of the cane stalk.

Extraction of the Soluble Bodies from the Chips.—A study was first made of the extraction of the sugars and other soluble bodies in the chips as follows: Twenty grams of chips taken from the comminuter were placed in a beaker, and nine volumes of water of varying temperatures added. The diffusates were polarized every fifteen minutes until the last two readings were the same.

The water in the beakers was kept as nearly as possible at the temperature of the water when added.

Results:

At	23° C.,	diffusion	complete in	65	minutes.
"	60° C.,	"	"	" 45-50	"
"	75-80° C.,	"	"	" 30-35	"

After pouring off the diffusate as completely as possible the above process was repeated in order to see if there was any appreciable difference in the rate of diffusion for the second application of water, but there was none.

From the polariscope readings of the completely diffused solutions the percentage of extraction of sucrose was calculated for the first two applications of water, and found to be seventy-five to eighty-five per cent. Assuming eighty per cent. for the average of each application of water, and twelve per cent. as the average amount of sucrose in the chips, after five complete diffusions of each sample there would remain in the chips only 0.0384 per cent. of sucrose, which is practically nil. Theoretically, ninety per cent. of the sucrose should be removed for each complete diffusion. In quite a number of cases the final diffusate was tested for sugars by means of the α naphthol reaction, which invariably showed only a very low percentage of these bodies.

The coagulation point of the water soluble albuminoids by heat was ascertained by gradually raising the temperature of the first diffusates till coagulation began, and found to be between 80 and 90° C. It is therefore unnecessary to begin the extraction by the addition of cold water, then warm water, etc., as is usually done. Since the diffusion is so much more rapid at high temperatures it is advantageous to begin by adding water at 75° C. for the first two diffusions, and boiling water for the last three, letting stand each time for thirty minutes. This can be safely done, as it will be seen, without fear of coagulating the albuminoids. This method was followed throughout the season.

Losses in the Preparation of the Samples.—In preparing samples for the estimation of the fiber in different parts of the cane, a portion of a cane stalk cut at the internodes with a sharp knife was rapidly weighed, ten grams cut off from both ends into a tared beaker, and the stalk reweighed, and was found to sus-

tain a greater loss than the ten grams cut off. This process was repeated in four cases, giving similar results.

Results:

No. 1.	Difference in weight after cutting off ten grams,	10.113
" 2.	" " " " " " " "	10.161
" 3.	" " " " " " " "	10.100
" 4.	" " " " " " " "	10.102

The chips were cut off in semi-circular pieces about $\frac{1}{16}$ of an inch in diameter. Sample 1, as soon as weighed, was cut finer with a pair of sharp scissors and rapidly weighed. It sustained a further loss of 0.107 gram, which added to the first loss makes a total of 0.22 per cent. while preparing the sample. These losses could not have been due in the main to evaporation, for the whole time occupied in preparing sample No. 1 was not over twenty minutes. Then Nos. 2, 3, and 4, were cut off early in the morning when the samples of 10 grams each lost by evaporation, for one hour, on an average 0.079 gram. The loss was more likely a mechanical one of the juice due to the rupture of the cells by the knife while cutting off the chips. If so, this loss would be augmented by the cutter and comminuter in the mill, especially so when the knives are dull.

Loss by Evaporation from the Chips.—According to well-known laws of physics the amount of evaporation varies with time of exposure, surface area exposed, and the temperature and humidity of the atmosphere. The fineness of the chips, which increases the surface, affects the rate of evaporation, probably also the ratio of the juice to the fiber. Upon the latter point I made no experiments. A piece of cane stalk, about an inch in diameter, was cut at the internodes, weighed, placed in the shade and reweighed at the end of each hour. The temperature at 12 o'clock 78° F., day dry.

Results:

12–1 P. M.,	loss by evaporation.....	0.48 gram.
1–2 "	" "	0.56 "
2–3 "	" "	0.40 "
3–4 "	" "	0.49 "
4–5 "	" "	0.52 "
Average loss each hour.....		0.49 gram.

This evaporation was mainly from the open ends and is therefore largely independent of the length of the piece of stalk.

Ten grams of chips were placed in a beaker in the room and weighed every hour, with the following results:

No. 1. From 10.30–11.30 A. M., loss by evaporation, 0.086 gram.
" 2. " " " " " " " 0.073 "
" 1. " 11.30–12.30 " " " " 0.269 "
" 2. " " " " " " " 0.266 "

The morning was very damp, there being a heavy fog which did not clear away until nearly 10 o'clock. From these results it would appear that quite an error may come from evaporation of the chips while the samples are accumulating at the mill, which often requires an hour or more. Add to this the mechanical loss from cutting the chips by the machine, and the error is sufficient to make the fiber appreciably high.

The Distribution of Fiber in the Cane.—These sources of error do not, of course, account for the differences in duplicate analyses. This error must be sought for in the difficulties in obtaining an average sample—in the variation in the fiber content in the different parts of the cane. To this end the following analyses were made: Ten grams of fiber were cut from the nodes, and ten grams from the contiguous internodes of the top, middle and butt of a stalk of purple cane, third year stubble of average size and weight, and the fiber estimated in these portions, giving the following results:

Top { Node..... 15.86 per cent.
Internode 8.60 " "

Middle { Node..... 15.9 per cent.
Internode 8.0 " "

Butt { Node..... 18.20 per cent.
Internode 8.08 " "

It will be noticed that there is approximately twice the percentage of fiber in the nodes as in the internodes, the butt node showing the highest percentage.

Fiber content in the rind and pulp of portions of cane stalk taken from the top, middle, and butt, cut so as to include a node and internode. (*a*) purple variety, plant cane; (*b*) purple variety, third year stubble.

		Rind.	Pulp.			Rind.	Pulp.
(*a*)	Top.....	26.0	8.7	(*b*)	Top.....	25.6	7.80
	Middle ..	29.5	6.5		Middle..	28.5	5.40
	Butt	28.5	6.8		Butt.....	28.5	5.77

Stubble cane always has a higher fiber content than plant cane of the same variety. From the above it would appear that this difference resides more in the pulp than in the rind.

It is difficult to say just what is rind and what is pulp in the cane stalk. So a portion of cane, about five inches in length, was cut from the center of a stalk of plant cane, purple variety, just within the two nodes. Ten grams of the rind was pared off into one beaker, ten grams taken off all round from what remained, and so on until the center of the stalk was reached, and the fiber estimated in these separate portions with the following results:

True rind	33.9	per cent.
Inside rind or bast tissue	13.33	" "
Next to inside rind	6.79	" "
Next to middle	4.77	" "
Middle	4.13	" "

The diffusate from the inside bark (bast cells?) was quite yellow, and it is probable that these cells furnish the yellow coloring matter in the expressed juice.

A joint of cane was cut just without the nodes, and the true node separated from that portion penetrated by the rootlets of the eye. Then ten grams were cut off from both ends of what remained at right angles to the length of the stalk, and an average of what remained was taken, and the fiber estimated in these portions, with the following results:

PURPLE VARIETY, THIRD YEAR STUBBLE.

Nodes proper	21.3	per cent.
Root nodes	14.2	" "
Next to the above	14.13	" "
Remaining internode	11.9	" "

From the above data it will be seen that the fiber varies very widely in amount in different parts of the cane, from 4.13 per cent. in the pulp to 33.9 per cent. in the rind. The percentage of what was considered as rind in the above analyses was estimated, and as an average of four cases was approximately twenty-one per cent. the weight of the cane. With such a difference in the fiber content of the rind and pulp, and such a percentage of rind, it is no small wonder that the duplicate analyses could not be brought to agree. For the presence of a very small undue proportion of rind or pulp in the samples would make the duplicates disagree. Often the knives of the cutters are dull, and strips of rind, varying in length, get into the chips. These, by the motion of the carriers, tend to accumulate on top, and are easily gotten hold of in undue proportion in the taking of the

sample. In such cases it is more difficult to get an average sample than when the chips are fine and regular.

LOSS OF GOLD AND SILVER DURING SCORIFICATION ASSAY.

By W. P. Mason and J. W. Bowman.

Received October 6, 1893.

NO explanation of the following numerical results is required, beyond stating that the losses referred to represent total losses, that is to say, losses due to both volatilization and mechanical causes. The furnaces employed were "Battersea No. F," and the conditions under which the assays were made, such as heat of muffle, draught in muffle, and manipulations in general, were such as would obtain in careful practical work.

SILVER.				GOLD.			
Weight before cupelling.	Weight after cupelling.	Loss.	Per cent.	Weight before cupelling.	Weight after cupelling.	Loss.	Per cent.
210.765	206.360	4.405	2.09	338.030	335.025	3.005	0.888
543.165	535.645	7.52	1.38	349.020	348.200	0.820	0.234
206.360	200.325	6.035	2.92	335.025	334.365	0.660	0.197
535.645	523.330	12.315	2.29	348.200	346.900	1.30	0.373
200.325	196.720	3.905	1.79	334.365	333.120	1.245	0.372
523.330	514.765	8.565	1.63	346.900	345.790	1.11	0.319
196.720	191.733	4.987	2.53	332.575	331.725	0.85	0.255
514.765	503.950	10.815	2.10	345.790	344.15	1.64	0.474
191.733	187.820	3.013	2.03	331.725	330.600	1.125	0.338
434.180	424.925	9.255	2.13	344.965	344.265	0.70	0.202
187.820	184.525	3.295	1.80	330.600	329.900	0.70	0.211
424.925	419.975	4.05	0.95	334.650	343.960	0.69	0.206
184.525	180.560	3.965	2.14	329.900	329.130	0.77	0.233
419.975	410.430	9.545	2.27	220.635	220.200	0.435	0.197
410.430	403.365	7.075	1.72	329.130	328.860	0.27	0.082
403.365	394.550	8.815	2.18	220.200	219.835	0.365	0.165
Average loss..... 1.99 per cent.				Average loss..... 0.296 per cent.			
" " entire process.. 2.54 " "				" " entire process 0.87 " "			
" " by cupellation.. 1.99 " "				" " by cupellation 0.296 " "			
" " in scorification. 0.55 " "				" " in scorification 0.574 " "			

SILVER.				GOLD.			
Weight before scorifying and cupelling.	Weight after scorifying and cupelling.	Loss.	Per cent.	Weight before scorifying and cupelling.	Weight after scorifying and cupelling.	Loss.	Per cent.
466.850	453.200	13.65	2.92	357.750	351.982	5.768	1.61
480.052	469.575	10.477	2.18	388.525	382.565	5.960	1.53
455.00	434.365	20.635	4.53	353.782	346.234	7.548	2.10
471.375	456.475	14.9	3.16	384.365	382.033	2.332	0.60
436.165	425.780	10.385	2.38	348.034	346.325	1.709	0.49
458.275	448.818	9.457	2.06	383.833	381.875	1.958	0.51
427.580	418.533	9.057	2.11	348.125	346.435	1.690	0.48
652.350	641.520	10.83	1.66	478.120	471.920	6.2	1.29
354.200	344.520	9.68	2.73	348.235	346.250	1.985	0.57
643.320	628.175	15.155	2.35	473.720	471.225	2.495	0.52
346.320	340.500	5.82	1.68	348.05	346.465	1.585	0.45
614.920	600.565	14.355	2.33	356.425	352.435	3.99	1.11
342.300	333.075	9.225	2.69	348.265	345.535	2.73	0.78
602.365	592.200	10.165	1.68	354.235	352.525	1.71	0.48
334.875	327.140	7.735	2.30	347.335	345.800	1.535	0.44
594.000	581.465	12.535	2.11	354.325	352.075	2.25	0.63
328.84	317.83	11.11	3.37	347.600	344.135	3.465	0.99
567.62	555.365	12.255	2.15	353.875	350.925	2.95	0.83
219.450	210.765	8.685	3.95	221.635	219.25	2.385	1.07
557.165	543.165	14.000	2.51	352.725	349.02	3.705	1.05
Average percentage loss.....2.54 per cent.				Average percentage loss.... 0.87 per cent.			

RENSSELAER POLYTECHNIC INSTITUTE,
1893.

ON THE SPEED OF REDUCTION OF FERRIC CHLORIDE BY STANNOUS CHLORIDE.

BY LOUIS KAHLENBERG.

Received February 8, 1894.

THE reaction that takes place when ferric chloride is treated with stannous chloride in aqueous solution is expressed by the following equation:

$$Fe_2Cl_6 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

This reaction goes on slowly enough at ordinary temperatures to admit of study from the standpoint of chemical dynamics. It was my purpose to investigate whether the reaction proceeds

in accordance with the law of mass action, as stated by Guldberg and Waage,[1] and how the speed of the reaction is affected by the presence of varying quantities of free hydrochloric acid.

Outline of Method of Experimentation.—Solutions of ferric chloride and stannous chloride of known strength were prepared. These were brought to a definite temperature by allowing them to stand in a bath. They were then quickly mixed (in equivalent proportions), and the mixture was kept at the same temperature in an atmosphere of carbon dioxide. At convenient times, samples were taken out with a pipette; these were quickly run into an excess of a saturated solution of mercuric chloride, which, by converting the unchanged stannous chloride into stannic chloride, according to the equation, $SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl$, checked the reaction. The amount of ferrous chloride formed was then determined by means of a standard solution of potassium bichromate. In this process, the bichromate was added until a drop of the mixture on a white porcelain plate showed no longer a blue coloration when brought into contact with a drop of a dilute, freshly prepared solution of potassium ferricyanide.

Preparation of Solutions.—A decinormal solution of potassium bichromate was prepared by taking 4.913 grams of the pure salt to a liter. Its strength was verified by comparison with both ferrous ammonium sulphate and iron wire. 17.85 cc. of this solution will change 0.1 gram of iron from the ferrous to the ferric state.

The ferric chloride used was of Merck's manufacture (C. P.). It was tested for arsenic and for sulphuric, nitric, and free hydrochloric acid, and found pure. Four liters of ferric chloride solution were prepared. The strength of this solution was determined by means of the decinormal bichromate solution, after previous reduction at a boiling heat with a slight excess of stannous chloride, and addition of an excess of mercuric chloride before titrating.[2] It was found that twenty-five cc. of the ferric chloride solution were equivalent to twenty-eight cc. of the bichromate.

[1] Études sur les affinités chimiques, 10, Christiania, 1867; also *J. prakt. Chem.*, [2], 19, 69.

[2] Kessler, *Pogg. Ann.*, 95, 223-225; also *Ztschr. anal. Chem.*, 11, 249.

Banca tin was used in preparing the solution of stannous chloride. The tin was found to be free from lead, iron, and arsenic. 30.5 grams of tin, to which a few scraps of platinum had been added, were heated with 125 cc. of hydrochloric acid of sp. gr. 1.17 in a flask in an atmosphere of carbon dioxide until nearly all the tin was dissolved. The heating had to be continued for about six hours. A little distilled water, previously boiled, was added from time to time so as to keep the volume of the liquid at about 100 cc. When the chemical action had ceased, about four to five grams of tin still remained undissolved. The excess of hydrochloric acid was driven off by boiling the liquid down to a small bulk. The stannous chloride thus obtained was diluted to 4,000 cc. with water previously boiled and cooled in an atmosphere of carbon dioxide. That the free hydrochloric acid had been driven off was evident from the fact that a precipitate of stannous oxychloride formed by diluting to this volume. It was found necessary to add to the four liters twenty cc. of hydrochloric acid, of sp. gr. 1.17, to bring this precipitate into solution. After this addition of acid and thorough shaking there still remained a faint opalescence, showing that a minimum quantity of acid had been used. The solution thus prepared was at once transferred to a number of flasks holding from 225 to 250 cc., about the quantity required for each series of experiments. The flasks were completely filled with the liquid, then tightly corked and kept in the dark. In this way the stannous chloride solution could be kept for weeks without changing, and the required quantity could be taken for use without exposing the remainder to the oxidizing influence of the air. The strength of the stannous chloride solution was determined as follows: Twenty-five cc. of the ferric chloride were acidified with hydrochloric acid and heated to boiling, twenty cc. of the stannous chloride were then quickly added and the amount of ferrous chloride formed at once estimated with the decinormal bichromate solution. In this way it was found that twenty cc. of the stannous chloride would reduce 18.7 cc. of the ferric chloride.

A saturated solution of mercuric chloride was also prepared.

Experimental Details.—In each of the six series of experiments

conducted, 200 cc. of the solution of stannous chloride and 187 cc. of the ferric chloride solution were used. The volume of this mixture was made up to 425 cc. for each series. In series I this was done by adding thirty-eight cc. of water, while in series II to VI, five, ten, fifteen, twenty, and twenty-five cc. of hydrochloric acid, of sp. gr. 1.17, at 20° C. respectively were added, together with an amount of water sufficient to make the volume up to 425 cc.

Preliminary experiments had shown that the speed of the reaction is greatly increased by raising the temperature and by increasing the amount of free hydrochloric acid present. The experiments were consequently carried out at 0° C., in order that the reaction might go on slowly enough to admit of the study of the increase of the speed of the reaction by the presence of the amounts of free hydrochloric acid above mentioned.

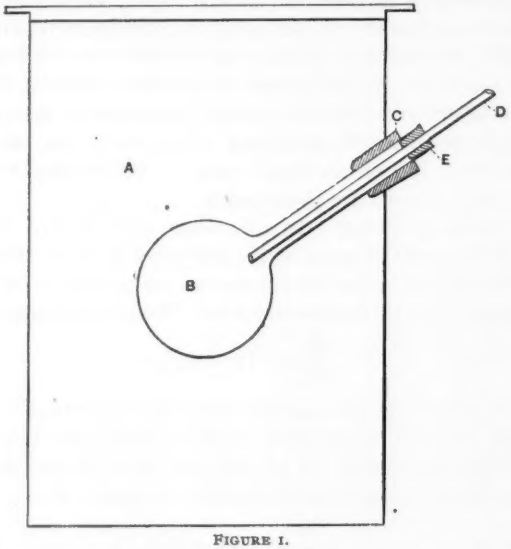

FIGURE 1.

Fig. 1 shows the apparatus in which the mixture of stannous chloride and ferric chloride was kept at 0° C. and in an atmosphere of carbon dioxide. The outer vessel A is made of tin and

has a capacity of about sixteen liters. It is provided with a wooden jacket and cover. The flask B has a capacity of about 500 cc. It is held in position by the tightly fitting rubber cork C which fits closely into the spout with which A is provided. The cork E fits loosely into the neck of the flask. The tube D is connected with a carbon dioxide generator.

At the beginning of each series of experiments, A was completely filled with melting ice and the air in the flask displaced by carbon dioxide. In the meantime the 200 cc. stannous chloride solution and the 187 cc. of ferric chloride solution, plus the thirty-eight cc. water—or water plus acid—were cooling in separate flasks in a bath of melting ice. When the solutions had been cooled to 0° C., they were quickly mixed and poured into the flask B, Fig. 1, the cork E being at once replaced. Samples of twenty-five cc. each were then taken out with a pipette from time to time, the cork E being slightly raised for the moment so that the pipette could be introduced into the flask B. These samples were quickly run into Erlenmeyer flasks containing fifteen cc. of the saturated mercuric chloride solution. The ferrous chloride formed was then estimated by means of the decinormal solution of potassium bichromate; the end of the reaction being judged as above stated. The results of the six series of experiments are given below.

Presentation of Results.—In accordance with the law of Guldberg and Waage, the speed of the reduction of ferric chloride by stannous chloride, when the substances are present in equivalent proportions, is to be expressed by the following equation:

$$\frac{dx}{dt} = c(a-x)^2, \qquad (1)$$

in which a represents the amount of substance present at the outset, x, the amount of substance changed during the time, t, and c, a constant depending on the concentration, temperature, etc.

From the above equation we have by integration:

$$\frac{1}{a-x} = ct + K. \qquad (2)$$

Determining K from the fact that x is zero when t is zero, and substituting its value in (2), we have after easy transformation,

$$\frac{1}{t}\frac{x}{a-x} = ac. \qquad (3)$$

The condition then that must be fulfilled, if the reaction follow the law, is that ac be constant.

The results of the six series of experiments are given in tabular form. Under t is given the time in minutes, counted, in the case of series I to V, from ten minutes after mixing the substances; while in series VI, five minutes after mixing was taken as the zero point from which to count the time. In the second column are given the amounts of the decinormal bichromate solution used in estimating the ferrous chloride formed. In series I the results of the titrations of two independent series of experiments are given under 1 and 2, while the average is given under 3. The last three columns of each series give the values of x, $\frac{x}{a-x}$, and ac, respectively.

For purposes of comparison, the results given in series I to VI have also been charted in the form of curves—Fig. 2. The abscissae represent the time in minutes, counting from the time of mixing, and the ordinates represent the amounts of ferric chloride reduced in percentages of the total amount present at the beginning. The numbers of the curves correspond to the numbers of the series.

SERIES I. (No free HCl present.)

t (minutes.)	$K_2Cr_2O_7$ (cc.)			x	$\frac{x}{a-x}$	ac.
	1	2	3			
0.....	1.3	1.25	1.27	...	.....	.....
10.....	2.1	2.3	2.2	0.93	0.0921	0.00921
20.....	2.9	2.8	2.85	1.58	0.1672	0.00836
40.....	3.7	3.7	3.7	2.43	0.2825	0.00706
60.....	4.2	4.2	4.2	2.93	0.3617	0.00603
80.....	4.8	4.6	4.7	3.43	0.4513	0.00564
100.....	5.25	5.2	5.23	3.96	0.5601	0.00560
120.....	5.6	5.6	5.6	4.33	0.6462	0.00539
140.....	6.0	6.0	6.0	4.73	0.7508	0.00536
190.....	6.6	6.4	6.5	5.23	0.9017	0.00475
250.....	7.25	7.3	7.27	6.00	1.1928	0.00477
320.....	7.6	7.6	7.6	6.33	1.3468	0.00421

(a = 11.03)

SERIES II. (Five cc. HCl present.)

t (minutes.)	$K_2Cr_2O_7$ (cc.)	x	$\frac{x}{a-x}$	ac.
0	2.95	...	.....	.....
10	4.45	1.50	0.1911	0.01911
35	6.55	3.60	0.6261	0.01789
50	7.1	4.15	0.7981	0.01596
70	7.6	4.65	0.9894	0.01413
80	7.95	5.00	1.1494	0.01437
110	8.5	5.55	1.4605	0.01327
140	8.95	6.00	1.7910	0.01279
170	9.3	6.35	2.1166	0.01245

(a = 9.35)

SERIES III. (Ten cc. free HCl present.)

t (minutes.)	$K_2Cr_2O_7$ (cc.)	x	$\frac{x}{a-x}$	ac.
0	5.55	...	.....	.....
10	7.1	1.55	0.2981	0.0298
20	7.95	2.40	0.5517	0.0276
30	8.5	2.95	0.7763	0.0259
40	8.95	3.40	1.0149	0.0254
50	9.2	3.65	1.1778	0.0236
70	9.65	4.10	1.5094	0.0216
100	9.95	4.40	1.8734	0.0187
120	10.15	4.60	2.1394	0.0178
150	10.45	4.90	2.6487	0.0177

(a = 6.75)

SERIES IV. (Fifteen cc. free HCl present.)

t (minutes.)	$K_2Cr_2O_7$ (cc.)	x	$\frac{x}{a-x}$	ac.
0	7.1	...	....	.....
10	8.5	1.4	0.368	0.0368
20	9.25	2.15	0.705	0.0352
30	9.7	2.6	1.000	0.0333
40	10.05	2.95	1.311	0.0328
50	10.35	3.25	1.667	0.0333
70	10.6	3.5	2.059	0.0292
80	10.75	3.65	2.355	0.0294
90	10.85	3.75	2.586	0.0287

(a = 5.2)

SERIES V. (Twenty cc. free HCl present.)

t (minutes.)	$K_2Cr_2O_7$ (cc.)	x	$\frac{x}{a-x}$	ac.
0	7.55	...	....	.....
10	9.15	1.6	0.508	0.0508
21	9.95	2.4	1.021	0.0486
50	10.8	3.25	2.167	0.0433
70	11.1	3.55	2.958	0.0423
95	11.35	3.8	4.000	0.0421

(a = 4.75)

SERIES VI. (Twenty-five cc. free HCl present.)

t (minutes.)	$K_2Cr_2O_7$ (cc.)	x	$\frac{x}{a-x}$	ac.
0.....	7.05	...	....	.....
10.....	9.25	2.2	0.721	0.0721
20.....	10.15	3.1	1.442	0.0721
25.....	10.40	3.35	1.763	0.0705
35.....	10.75	3.7	2.387	0.0682
50.....	11.00	3.95	3.038	0.0608
70.....	11.25	4.2	4.000	0.0571
100.....	11.45	4.4	5.176	0.0518
130.....	11.55	4.5	6.081	0.0468

(a = 5.25)

It will be noticed that the quantity ac, instead of being constant, decreases in each series. In eight preliminary series of experiments, performed at 0° and at 15° to 16°, the same regular decrease of ac was noted. The cause of this retardation of the speed of the reaction has not been further investigated. It seems probable that it is due to the accumulation of the products of the reaction (stannic chloride and ferrous chloride), and to the change in the rate of diffusion as the solution becomes more dilute. It must be observed, however, that while the first values of ac in each of the six series given above are too high, owing probably to disturbing influences at the beginning of the experiments, the values at about the middle of the series vary but slightly indeed, in many instances the differences fall within the limit of error of experimentation. The results above given are sufficient to show that the reaction follows the law of Guldberg and Waage fairly well.

The effect of the presence of varying quantities of free hydrochloric acid on the speed of the reaction can best be seen by comparing the curves in Fig. 2. All the curves show that the reaction goes on most rapidly during the first ten to fifteen minutes after mixing.[1] During the first forty minutes after mixing, the second five cc. hydrochloric acid (curve III) increases the amount of ferric chloride reduced in about the same degree as does the first five cc. (curve II); but this effect diminishes relatively as the time increases. In general, the curves show that as the amount of free hydrochloric acid is increased the effect on

[1] This effect has in part been eliminated in preparing the tables above, by choosing ten minutes after mixing as the zero point from which to count the time.

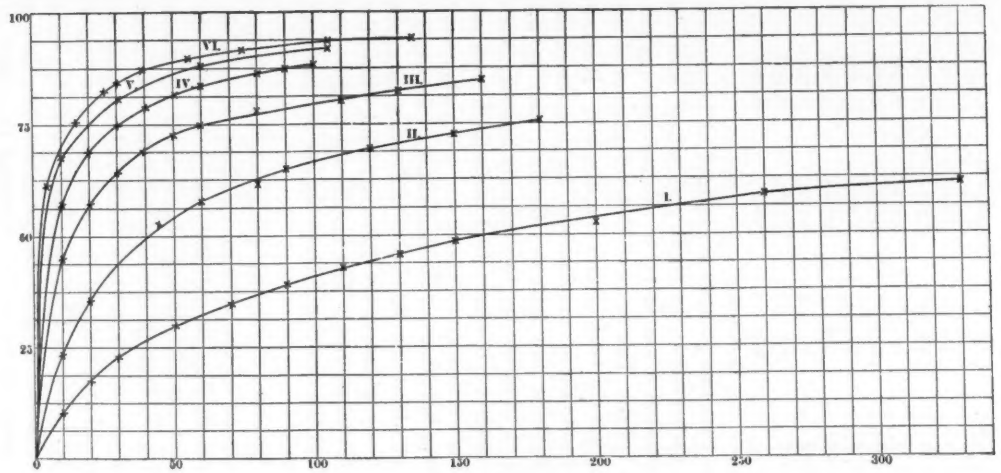

FIGURE 2.

Abscissae = Time in minutes.
Ordinates = Amount of $FeCl_3$ reduced in per cent.
Curve I, no free HCl is present.
" II, 5 cc. free HCl is present.
" III, 10 " " " " "
" IV, 15 " " " " "
" V, 20 " " " " "
" VI, 25 " " " " "

amount of ferric chloride reduced is relatively diminished.

Curves similar to those in Fig. 2 have lately been obtained by Seubert and Dorrer[1] in the case of the action of ferric chloride on potassium iodide. Their curves show the effect of the presence of an excess of either substance on the speed of the reaction.

In the case of the reduction of ferric chloride by stannous chloride, the part played by the free hydrochloric acid cannot be expressed in the form of a chemical equation; and as there can be no doubt that the amount of free acid present at the end of the reaction is the same as at the beginning, the action of the acid is catalytic in its nature. In the course of his investigations of processes of oxidation and reduction, Prof. Ostwald[2] has formulated the law that the speed of all processes of oxidation and reduction is increased by the presence of free acids in proportion to their affinity coefficients. He has shown that this law holds also in cases of catalytic action. It would be of interest in this connection to know the effect of the presence of equivalent quantities of other acids on the speed of the reduction of ferric chloride by stannous chloride; but as another problem required my immediate attention, the work could not be continued in this direction.

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CHEMICAL LABORATORY OF THE
UNIVERSITY OF WISCONSIN.

THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND CEMENT.

(*Continued from Page 286.*)

BY THOMAS B. STILLMAN, PH.D.

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[1] *Ztschr. anorg. Chem.*, 5, 348 and 352, *1893*.

[2] *Ztschr. phys. Chem.*, 2, 127.

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[TO BE CONTINUED.]

CREAM OF TARTAR SUBSTITUTES: THEIR CHEMISTRY AND ANALYSIS.

By W. E. Wadman.

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TO make an intelligent analysis of any complex substance, the chemist must possess not only the requisite skill, but also a certain amount of knowledge of the material he is working with, in order that the bare analytical results may be correctly interpreted, and given their proper meaning in relation to the particular substance yielding them.

Among the substances with which the majority of practicing chemists appear to be little familiar, is the class of products known in trade under the generic name of cream of tartar substitutes.

Under this general name are included a great many acid powders which are used to replace cream of tartar in the manufacture of baking powders, self-raising flours, and also directly in baking, their function being always that of an acid to liberate carbonic acid gas from sodium bicarbonate.

All cream of tartar substitutes have the common feature that their active acid element is primarily monocalcium phosphate, ($CaH_4P_2O_8$), but in other respects they differ so widely in composition and function, that for convenience in considering them it is best to divide them into two primary classes or types.

The first class (hereafter referred to as class I) consists of goods prepared by treating calcium phosphate (in practice usually in the form of boneblack) with sufficient sulphuric acid to produce monocalcium phosphate and calcium sulphate, filtering off the sulphate, evaporating the solution of monocalcium phosphate to crystallization, mixing with starch, drying and grinding. The resulting product is chiefly a mixture of monocalcium phosphate with starch, but invariably contains a small amount of "free" or uncombined phosphoric acid (varying from one per cent. to six per cent. P_2O_5), and also a considerable quantity of insoluble phosphates, chiefly calcium but frequently iron and aluminum phosphates also. Tartar substitutes of this class are frequently known in trade as "Leached goods."

The other primary type (hereafter referred to as class II) differs from the preceding in method of manufacture, in chemical composition and also in its use and behavior.

The raw material is carefully prepared, pure white bone ash which is treated with the requisite amount of concentrated sulphuric acid, and the resulting mixture, monocalcium phosphate and calcium sulphate, is dried and ground without separation. Hence goods of this type contain a large amount of calcium sulphate, equivalent to the amount of sulphuric acid used in their preparation, and are frequently referred to as "sulphate of lime base" goods.

The essential difference between the two principal types is, that one is practically free from calcium sulphate, while the other contains a large amount of this salt.

Like class I the goods of the second class almost always contain a small amount of free phosphoric acid, and generally considerable quantities of insoluble phosphate, chiefly tricalcium. As a rule they contain very little starch, and frequently none at all.

With regard to this content of calcium sulphate in goods of the second class, it is a common mistake of chemists who are not familiar with these materials, to stigmatize it as an "adulteration," or "the result of careless or imperfect manufacture." Such statements are entirely erroneous, as the calcium sulphate is an essential part of the goods and has a very important influence on their action, as explained later.

A point to be noticed, which is a stumbling block to many chemists, is the simultaneous occurrence of free phosphoric acid and insoluble phosphates. It is usually supposed that these two substances in contact will at once react to produce monocalcium phosphate ($Ca_3P_2O_8 + 4H_3PO_4 = 3CaH_4P_2O_8$) and I have seen the statement, over the name of a well-known chemist, that "free phosphoric acid and insoluble phosphates cannot exist together." As a matter of fact the above reaction, like many others, is seldom, and only under exceptional circumstances, complete, and free phosphoric acid and insoluble phosphates not only can, but almost invariably do co-exist in tartar substitutes. This fact has an important bearing on the analysis of these substances.

As examples of the composition of the two extreme types above described, the following analyses may be given:

	Class I.	Class II.
Moisture	4.41	2.42
Monocalcium phosphate (crystallized)	49.67	29.48
Monomagnesium phosphate (crystallized)	2.75	3.54
Free phosphoric acid (hydrated)	2.02	0.73
Insoluble calcium phosphate	13.08	8.66
Calcium sulphate (anhydrous)	0.85	48.70
Silica, etc.	0.3	0.13
Starch	26.00	3.27
Alkaline salts, water of crystallization, and undetermined	0.92	3.07
	100.00	100.00
100 lbs. will neutralize sodium bicarbonate	45 lbs.	{ cold 27½ / hot 48½

There are many grades in the market intermediate between these, prepared for special uses, but which may practically be regarded as mixtures of these two principal types.

Effect of Chemical Composition on the Character and Practical Behavior of the Goods.

Class I.—The acidity or neutralizing power of this class is entirely due to the monocalcium phosphate and the free phosphoric acid, the exact nature of the reaction with soda varying with the conditions of temperature, dilution, etc., etc., but mainly resulting in the production of dicalcium phosphate $Ca_2H_2P_2O_8$ and disodium hydrogen phosphate.

Both monocalcium phosphate and phosphoric acid being readily soluble substances, the reaction takes place practically to the same extent in hot or cold solution.

With goods of the second class, *i. e.*, containing calcium sulphate, the reaction with soda is quite different. The primary reaction of the monocalcium phosphate on the sodium bicarbonate is the same as in the foregoing, but on heating, a secondary reaction occurs between the calcium sulphate and the products of the primary reaction, probably thus: $3Na_2HPO_4 + 3CaSO_4 = Ca_2P_2O_8 + 3Na_2SO_4 + H_3PO_4$, which it will be seen, is equivalent to liberating a fresh quantity of acid. In other words, the presence of calcium sulphate compels the phosphoric

acid to do more work, and the final product is tricalcium instead of dicalcium phosphate.

This secondary reaction only takes place on heating, and is the more complete the longer the mixture is boiled. The practical effect of this in the use of tartar substitutes is of very great importance.

Goods of class I, whose neutralizing power depends entirely on their contents of monocalcium phosphate and free phosphoric acid, when mixed with sodium bicarbonate and water, liberate the carbonic acid gas at once and completely in the cold; and hence, if this combination is used in baking, it is necessary that the dough should be placed in the oven immediately after mixing, as otherwise the gas escapes and the resulting loaf is "heavy."

With goods of class II, on first mixing the dough a portion only of the gas is liberated (corresponding to the primary reaction), making the dough spongy, but on putting in the oven, the secondary reaction commences and a steady evolution of gas occurs, which keeps the loaf porous and light.

This two-fold reaction has, in fact, the same practical effect as is obtained by the use of a less readily soluble salt than monocalcium phosphate; *viz.*, the action is slower.

The special suitability of cream of tartar for baking powder purposes rests on its property of being only sparingly soluble in cold water, but quite readily so in hot water, the effect of which is that the carbon dioxide is developed in the right amounts at the right time; exactly the same result is obtained in tartar substitutes by means of the secondary reaction with calcium sulphate.

The calcium sulphate in some tartar substitutes cannot, therefore, be regarded as an adulterant, neither is it the result of carelessness on the part of the manufacturer; but it purposely forms part of the substance, and has an important, and for some uses, quite an essential function.

It is not my purpose at present to treat the matter from a hygienic point of view, but, inasmuch as calcium sulphate seems to be something of a bugbear to many health officers and state chemists, it may be pointed out that a greater part at any rate of this substance is actually converted in the baking process

into sodium sulphate, and further, that in the small amounts used in practical baking the resulting dose of the latter salt would be extremely small.

Analysis of Tartar Substitutes and Statement of Results.

It might at first sight seem supererogatory to detail any methods of analysis of a material composed of such familiar substances as lime, phosphoric and sulphuric acids, magnesia, etc., etc., still more so to enter into a matter apparently so simple as the determination of the neutralizing power of an acid substance.

The determination of the working power of tartar substitutes, however, presents peculiar difficulties, so much so that an analyst inexperienced as regards these materials as a rule fails entirely to get results of any value whatever, and as regards the more complete analysis, the determinations of lime, phosphoric acid, etc., etc., indeed present no difficulty. But when the attempt is made to group the acids and bases, it frequently results in surprising misstatements.

A matter of primary importance in the analysis of tartar substitutes is the determination of the "strength," or neutralizing power, always stated in terms of sodium bicarbonate.

To determine this "strength," two obvious methods present themselves; *viz.*, titration with standard alkali, and the determination of the amount of carbon dioxide evolved from sodium bicarbonate by a known weight of the substance. Inasmuch, however, as the indications given by the above two processes are two entirely different things, it must first be decided before adopting one or the other method, exactly what is meant by "strength" in a powder of this kind.

When monocalcium phosphate and sodium bicarbonate are heated together in presence of water, the carbonate is decomposed until the salt Na_2HPO_4 is formed. This salt, although chemically "acid," is already strongly alkaline to phenolphthalein, the salt of the formula $R_3H_3P_2O_8$ probably being the neutral salt to this indicator. It is obvious, therefore, that "acidity" of tartar substitutes, as indicated by titration, is quite a different matter from their ultimate power of determining the liberation of carbon dioxide from carbonates.

Ordinarily, for reasons above given, the "evolution" method indicates a power of evolving carbonic acid gas very considerably in excess of the "acidity" as indicated by titration. Unfortunately, however, both methods offer ample opportunity for error.

When a mixture of acid phosphate and sodium bicarbonate is heated with water, the amount of carbon dioxide evolved is dependent on the relative proportions of the two substances, on time, temperature, dilution and a host of other factors; and, by varying the conditions, results can be obtained differing from each other and the truth, not slightly, but to an extent to render the test useless.

In an article on the "Commercial Valuation of Cream of Tartar Substitutes," *J. Anal. Chem.*, **4**, 4, Prof. Chas. A. Catlin sums up the foregoing in the words "there is found to be no definite ratio between the neutralizing capacity of these preparations and their gas-evolving power when in admixture with alkaline bicarbonate under the conditions of the baking process," and advocates the use of a modified form of the evolution method on the ground that inasmuch as the use of these powders is to evolve carbonic acid gas from alkaline bicarbonate, their power of doing this under the conditions of the baking process is the sole criterion of value.

There is, however, another factor that must be considered; *viz.*, the reaction of the residue. It is no less necessary that a baking powder shall have a neutral residue, than that it shall evolve carbonic acid gas, and there is this much in favor of the titration method, that if properly conducted it indicates exactly the amount of sodium bicarbonate that can be used with a given sample of tartar substitutes to give a neutral residue.

I can quite endorse Prof. Catlin's statement, that the ordinary method of titration with alkali, either direct or indirect, fails to give the proper data, but if the titration is conducted with special precautions, adapting it to the case, it is in my opinion the most satisfactory method of determining the "strength" of tartar substitutes.

The method of valuation proposed by Prof. Catlin is a combination of the titration and evolution methods; *viz.*, first find-

ing by titration with alkali and phenolphthalein the neutralizing power of the sample, and then weighing up exactly the amount of chemically pure bicarbonate, introducing into the evolution apparatus together with its equivalent of tartar substitutes, and weighing the carbon dioxide evolved under certain specified conditions.

It would seem that the evolution part of this method is entirely dependent on the titration, for certainly, if, in the evolution experiment only the exact equivalent of sodium bicarbonate as found by titration is used, the carbon dioxide corresponding to this and no more can possibly be evolved, and inasmuch as under the conditions laid down by Prof. Catlin for the evolution experiment, nearly all tartar substitutes will evolve carbon dioxide from more bicarbonate than is indicated by a properly conducted titration, the evolution experiment can at best only confirm the titration, and had better be altogether dispensed with as a troublesome and useless adjunct.

Prof. Catlin's paper contains many extremely valuable data as to the actual conditions to which the leavening agents are exposed in the practical baking process, and as emphasizing the necessity of making analytical tests as nearly as possibly under these conditions, is well worthy of attention.

The method of conducting the titration test differs with the character of the sample to be tested.

In the case of tartar substitutes of class I (*i. e.*, practically free from calcium sulphate) the amount of alkali neutralized is practically the same whether the titration be conducted hot or cold.

With class II, or intermediate grades containing any considerable amount of calcium sulphate, this is not the case, for when titrated in the cold, the solution reacts alkaline to phenolphthalein as soon as the primary reaction between soluble phosphoric acid and soda is complete. If now this solution be heated, the secondary reaction, previously explained, commences; the red color of the phenolphthalein gradually disappears, till on full boiling it will be found that a very considerable amount of alkali must be added before neutrality is restored. Hence, tartar substitute containing calcium sulphate shows one strength cold and a much greater strength hot; or, as it is expressed in trade, "sulphate of lime base goods show a *cold* test."

As before stated, in the case of goods free from calcium sulphate, the "hot" and "cold" tests are identical, or they "have no cold test."

It will be understood that the difference between the hot and cold test is purely a function of the secondary reaction with calcium sulphate, and from the relation between the two tests an expert can form a tolerably close estimate of the amount of this substance present.

To return to the titration, the test is best made on one gram of the substance suspended in about thirty cc. water in a porcelain basin, and titrating with caustic alkali (carefully freed from carbon dioxide), using phenolphthalein as indicator. The one essential of the method is to use a very large amount of the indicator. If the titration is made using only one or two drops of phenolphthalein, as would ordinarily suffice for an acidimetric titration, a far larger amount of alkali can be added, before the faintest pink color is obtained, than is really required. This may be readily shown by adding a further considerable amount of phenolphthalein when the faint pink darkens to deep red, and on titrating back with acid a considerable amount must be used before the color disappears. For this reason an inexperienced operator always obtains results far too high.

The most convenient method of procedure when working with unknown samples is, first to make a cold titration, adding a large amount of phenolphthalein and titrating to a faint pink. The alkali should be added drop by drop with constant and vigorous stirring to break up the little clots of precipitated phosphates formed by each drop.

In the case of sulphated goods the first pink tinge indicates the "cold test" and the burette reading should be recorded. The solution is then rapidly brought to a boil under the burette, and if the pink disappears more alkali is added till the very faintest color reappears.

This first test serves as a guide for a more exact titration in which it is best to add nearly the full amount of alkali required, drop by drop as before, then bring to a brisk boil, add the phenolphthalein and finish the titration rapidly while still actively boiling. The ending should be the first faint pink permanent

for one minute at a boiling temperature. The end reaction is not sharp and is very difficult to determine exactly.

With heavily sulphated goods prolonged boiling will cause the pink to disappear owing to the greater completeness of the secondary reaction; but as Prof. Catlin has pointed out, in the baking process the chemicals are exposed to a temperature of 100° for a period not exceeding one minute at the most, and therefore in the test this time of boiling should not be exceeded.

Any process of indirect titration, by adding alkali in excess and titrating back with acid is entirely inadmissable, as is also any separation of the insoluble portions of the powder by filtration before titrating.

The more complete analysis of a tartar substitute involves the determination of the phosphoric acid, and *the forms in which it exists*, the lime, magnesia, starch, sulphuric acid, and occasionally iron and alumina.

The determination of these substances requires no special notice, except as regards the forms in which the phosphoric acid exists, which is a matter of the highest importance in determining the relative merits of tartar substitutes.

Disregarding the small amounts combined with magnesia, iron, and alumina, the phosphoric acid in tartar substitutes is present in three different states:

"Free," or uncombined.

Combined with one molecule of lime, as $CaH_4P_2O_8$.

Combined with more than one molecule of lime as insoluble phosphates; and in order to make an analysis of any value whatever, it is absolutely necessary to determine the amount present in each of these forms.

The "free" acid may be determined by titration with standard alkali and methyl orange, which indicator reacts neutral with salts of the formula $R'H_2PO_4$, and consequently indicates the "free" phosphoric acid only.

The titration is best effected on the filtered aqueous solution, adding standard alkali to pink-yellow color. Inasmuch as a slight precipitate forms before the point is reached the indications are a trifle too high, but sufficiently accurate for all technical purposes.

For the determination of the phosphoric acid existing as monocalcicum phosphate and insoluble phosphates two analyses are necessary.

First, the *total* phosphoric acid on the solution of the powder in acid, and secondly, the "water soluble" phosphoric acid, best extracted by shaking a weighed quantity with water in a graduated flask, filtering clear and determining the dissolved phosphoric acid in an aliquot of the filtrate.

The phosphoric acid can of course be determined by any orthodox method, but for convenience and rapidity the volumetric method of Pemberton, (this JOURNAL, July, *1893*) far surpasses any other.

The total phosphoric acid minus the "water soluble" gives the "insoluble" phosphoric acid, which may exist as $Ca_3P_2O_8$, $Ca_2H_2P_2O_8$, or frequently as a mixture of the two. The determination of the insoluble phosphoric acid by difference is far more satisfactory than a direct determination.

The "water soluble" minus the "free" equals phosphoric acid existing as $CaH_4P_2O_8$.

It is necessary here to call attention to a very vicious practice followed by some chemists. Instead of determining the three forms of phosphoric acid as above, they determine only the *total* phosphoric acid and the total CaO. The CaO they then calculate into $Ca_3P_2O_8$, an excess of phosphoric acid of course remaining uncombined—which excess they then combine with the $Ca_3P_2O_8$, according to the reaction $Ca_3P_2O_8 + 4H_3PO_4 = 3CaH_4P_2O_8$, leaving an excess of either $Ca_3P_2O_8$ or H_3PO_4 as the case may be, but necessarily showing only one or the other.

Such a calculation cannot by any chance give correctly the composition of the substance for the reason before gone into, that tartar substitutes always contain both free acid and insoluble phosphates.

One word as to the form of stating results may not be out of place as this is a frequent source of *apparent* disagreement between two analyses that are really identical—a matter that it is often difficult to satisfactorily explain to the lay mind.

Having found, correctly or otherwise, the amount of monocalcium phosphate present in a sample, the analyst generally

states this in his report in the anhydrous form, $CaH_4P_2O_8$, calling it variously "monocalcium phosphate," "acid phosphate of lime," and occasionally "superphosphate," or some other name.

Equally in the case of calcium sulphate, it is a usual practice to report in the anhydrous form $CaSO_4$, and to call it variously "sulphate of lime," "gypsum," "terra alba," "plaster of Paris," etc., etc., according to the state of mind of the analyst. Even the starch present in tartar substitute is capable of being reported under the misleading term of "organic matter."

Having reported the salts as present in their anhydrous state, the difference between the sum of results and 100 is put down as "combined water," etc., etc.

While such a method of reporting is very convenient, as saving trouble of calculation and giving a pretty analysis adding up exactly to 100.00, it is doubtful if it is the best way.

In my opinion the results of an analysis should always be reported in a form as nearly approaching the truth as may be, and at any rate the statement should always show on the face of it exactly what is meant.

In the case in point, monocalcium phosphate always exists (and indeed can only exist) in a crystallized state, and in consequence it would seem to better represent the truth if stated in this form and called "crystallized monocalcium" or "acid phosphate."

With regard to the calcium sulphate in highly sulphated goods, it appears to exist partly in the anhydrous state and partly crystallized, and as it is impossible to determine the amount of water of crystallization, the exact statement of this cannot be made. It is, however, easy to convey exactly what is meant by stating either as "anhydrous" or "crystallized" calcium sulphate.

The practice of calling calcium sulphate found by analysis "terra alba," "gypsum," etc., etc., is to be unqualifiedly condemned, as it suggests, and is intended to suggest by implication, a fraudulent addition of a foreign substance,—a suggestion that is justified neither by the analytical data nor the real facts of the case.

The neutralizing strength should always be stated in terms of

sodium bicarbonate neutralized by 100 parts of the sample, and where there is a considerable difference between the hot and cold tests, this should be stated, as it is an important factor in deciding as to the suitability of a tartar substitute for any particular use.

The best grades in the market have a neutralizing strength of 100 parts equivalent to forty-four to forty-five sodium bicarbonate, *i. e.*, about the working strength of cream of tartar.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE, NO. 3.]

THE ANALYSIS OF VARNISHES.

BY PARKER C. MCILHINEY, PH.B., A.M.

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AT present varnishes are seldom analyzed because no means are known of determining with any approach to accuracy, the amounts of the substances composing them. The tests used are practical ones and usually consist in varnishing a suitable surface with the sample to be tested and subjecting the varnished object to treatment as nearly as possible like that which it will receive in practice. If it is desired to ascertain the proportions of the different constituents, practical varnish-makers claim to be able to make up samples which will match in properties one to be tested, and in this way to arrive at the proper result. However this may be, it is out of the question for the chemist who is not a varnish-maker to use such a process. If methods can be devised whereby a chemist can make an actual analysis with a fair degree of accuracy, buyers can be certain of what they purchase and manufacturers can work more intelligently.

The different kinds of varnish may be classified as follows:

1. Spirit varnishes.
2. Volatile oil varnishes.
3. Fixed oil varnishes.
4. Miscellaneous; collodion varnishes, etc.

Spirit varnishes are composed of a resin dissolved in alcohol. Shellac spirits, made by dissolving shellac in wood or grain alcohol, is the most common.

Volatile oil varnishes are made by dissolving a resin in turpentine. Dammar varnish is a good example. Benzine is largely used as a substitute for turpentine in this and other varnishes.

The most important class is the fixed oil varnishes, and it is the analysis of this sort which will be considered. They are made from linseed-oil, a resin, and turpentine.

The principal resins used are kauri, manilla, and hard copals, such as Zanzibar. Common rosin is largely used as an adulterant. Kauri is the resin used by far the most, and there are many grades, varying in price from three cents to sixty cents a pound. Manilla stands next in the amount used, and of the others comparatively small quantities are used.

The resins used in fixed oil varnishes are in their natural state insoluble in linseed-oil and in turpentine. It is only after undergoing a process of roasting or distillation that they become soluble, and in this operation they loose from twenty to twenty-five per cent. in weight. In the process of manufacture the resin is first melted down in a kettle, and after it has been sufficiently heated the proper quantity of linseed-oil, also hot, is added, and the mixture heated some time longer to effect a combination between the oil and resin. After cooling somewhat, sufficient turpentine is added to properly thin the varnish.

It is difficult for several reasons to obtain samples of varnish for experiment in which the proportion of the constituents is known. They cannot be made successfully in small quantities as they are then of poor quality, and results obtained from such samples cannot be trusted. Through the kindness of Prof. A. H. Sabin, three samples of varnishes of known composition were obtained for experiment.

The Determination of Turpentine.—H. J. Phillips (*Chem. News*, **63**, 275, and *J. Soc. Chem. Ind.*, **10**, 577) proposes to distill off the turpentine at 220° C., using about 150 grams of varnish and catching the distillate in a tared flask. A current of coal-gas is passed through the liquid to prevent oxidation of the linseed-oil, and at the same time to assist in the removal of the turpentine vapor by carrying it away as fast as formed, and by agitating the liquid. The method is open to several objections; any vapors of naphtha in the coal-gas used are likely to be caught

and contaminate the turpentine. This difficulty would be overcome by the use of carbon dioxide instead of coal-gas, but carbon dioxide is not usually available in sufficient quantity. The author does not use any condenser, but depends upon the cooling of the neck of the retort used by the air, which is not sufficient. The residue left after most of the turpentine is gone is very viscous and retains some turpentine very persistently.

Mills (*J. Soc. Chem. Ind.*, **5**, 222) says that the volatile constituents of varnish are easily determinable by evaporation with water.

Attempts were made to effect the removal of turpentine by distilling it off in a vacuum. Trials were first made using twenty-five grams of substance and a temperature of 100°–120° C., but this proved to be much too low a temperature and it was subsequently found that by using five grams instead of twenty-five grams of substance the results were better.

The method used was as follows: A portion of the varnish is weighed into a tared, round-bottom flask which is then heated in a paraffin bath at a temperature of 180° C. for four to eight hours, the air and vapor being removed from the interior of the flask by a pump. The flask is then again weighed and the loss in weight represents turpentine.

The results by this method were as follows:

Varnish used.	Per cent. of turpentine found.	Per cent. present.	Quantity of substance used.
A	52.7	60.0	25 grams.
B	34.9	41.4	25 "
C	52.7	56.9	5 "

The results are thus seen to be too low and irregular, and the residues smelled of turpentine. It was found that these traces of turpentine could be removed, and correct results obtained by adding to the contents of the flask after cooling two or three cc. of petroleum ether of very low boiling-point, allowing the residue to dissolve, and then carefully exhausting the flask of air, and finally heating gently. Of course, in these experiments it is necessary to use round-bottom flasks. The great objections to this method are that it does not distinguish between turpentine and any other volatile substance, and also that it requires arrangements for exhausting air, which are not always available. The

non-volatile residue is, however, in the very best condition for further examination.

Another method which has been used is a determination of the loss in weight on evaporating off the turpentine in the air-bath at 100° C. from a quantity of varnish contained in a watch-glass. This method is open to the same objections as the previous process, and the residue is not in good condition for further examination on account of the drying of linseed-oil. The fact that linseed-oil increases in weight on exposure to the air tends to give too low results. The formation of a film of dried varnish preventing further evaporation renders it necessary to use only small quantities of substance. In experimenting with the process it was found better to use watch-glasses of flat form than the ordinary concave ones. Three-quarters to one hour exposure at 100° and 0.400 to 0.500 gram substance gave the best results.

The following figures were obtained in this way:

Varnish.	Amount found.	Amount present.
B	40.8	41.4
C	56.0	56.9
D	53.4	56.8

The requirements of a satisfactory process for determining turpentine are:

(1) That the volatile material shall be separated under conditions which admit of its being actually weighed or measured and then submitted to further treatment.

(2) That the non-volatile portion shall be subjected to as little heat as possible, both to avoid any destructive distillation and to leave it unaltered for further examination.

(3) The process should require no unusual apparatus. None of these processes fulfill the above conditions.

It is well known that on distilling together two immiscible liquids, such as carbon disulphide and water, the boiling-point of the mixture is lower than that of the more volatile liquid. Carbon disulphide boils at 49°, but when distilled with water the boiling-point of the mixture is 43° (Kundt, *Jahresb. Fort. Chem.*, *1870*, 49).

On distilling together 100 cc. of water and five cc. of turpentine it was found that the first ninety-five cc. of distillate contained all the turpentine which separated very well from the

water. Experiment showed that ninety cc. of water either dissolve or hold in suspension permanently about 0.3000 gram of turpentine. On these principles the following process was devised:

Twenty-five grams of varnish are weighed into a flask of 400 cc. capacity, in which has been placed a piece of granulated tin, or its equivalent, to prevent bumping and about ten cc. of water. The flask is in this way prevented from becoming greasy, which would cause violent bumping. The contents of the flask are now submitted to distillation, the distillate being caught in a tapped separator. When ninety or ninety-five cc. of water have come over, the distillation is stopped and the turpentine and water allowed to separate. If the contents of the flask still retain any odor of turpentine more water should be added and the distillation resumed. After settling for a sufficient length of time, the water is carefully drawn off and the turpentine poured into a tared flask and weighed. A correction is made for the amount of turpentine retained by the water, amounting to 0.300 gram for ninety cc. of water. In some experiments salt was added to the water to raise its boiling-point, but no apparent advantage was gained except when the non-volatile residue was heavier than water; in this case the salt prevented the residue from sinking to the bottom and causing bumping by greasing the flask. If it is desired to examine the residue, the remaining water is poured off from it and alcohol added. On distilling off the alcohol, and if necessary removing the last of it by the addition of a little ether, which is also evaporated off, the residue is obtained pure.

The following results were obtained by this process:

Varnish.	Per cent. found.	Per cent. present.
B	41.2	41.4
C	57.1	56.9
D	56.3	56.8

The sample D was made by dissolving common rosin in turpentine, and it was therefore more difficult to remove the last trace of turpentine from the non-volatile residue than it ever is in an oil varnish, but even in this case the result is fairly accurate.

The method requires no unusual apparatus and can be carried out in about half an hour. The residue is not heated above the

boiling-point of water, and the turpentine is actually weighed and may be itself analyzed.

For the determination of benzine in turpentine, the method of Burton (*Am. Chem. J.*, **12,** 102) gives the best results. It depends upon the conversion of turpentine into acids soluble in water by the action of nitric acid while benzine remains unaffected and is separated and measured or weighed.

The Non-volatile Portion.—The analysis of the residue consisting of linseed-oil and resin, both more or less altered by heat, presents an extremely difficult problem in proximate analysis and one which yet remains unsolved.

The properties of resins have been investigated analytically by;

Hirschsohn, *Pharm. Ztschr. f. Russland*, *1875*, 225, and *1877*, 1; *Pharm. Jour.*, **7,** 369, and **8,** 389.

Schmidt and Erban, *Sitz. d. Wiener. Akad.*, **94,** 917, and *Ztschr. angew. Chem.*, *1889*, 35.

Mills, *J. Soc. Chem. Ind.*, **5,** 222.

Mills and Muter, *J. Soc. Chem. Ind.*, **4,** 96.

Williams, *Chem. News*, **58,** 224.

These investigators have made upon various resins the same tests which have been used in the analysis of oils; *viz.*, the acid figure, the Koettstorfer figure, the iodine figure, the per cent. of bromine absorbed, and the solubility in ether, alcohol, etc. Their results are given in the following table:

Resin.	Variety.	Acid figure.	Koettstorfer figure.	Hübl figure.	Per cent. bromine absorbed.	Observer.
Amber		15.4	86.8	62.1	.....	Williams.
"		....	160.7	.....	53.53	Mills.
"		....	145.0	.....	.....	Schmidt and Erban.
"		....	144.6	.....	.....	" " "
"	Melted	0.0	38.9	4.8	.....	" " "
"	"	0.0	33.9	.....	.....	" " "
Animé	Rough Demarara	26.6	73.6	127.88	.....	Williams.
"	Fine Zanzibar	18.2	73.6	135.25	.....	"
"	Unknown	25.2	87.5	137.54	.....	
"		....	95.4	.....	60.22	Mills.
Copal	Soft manilla	131.6	184.1	137.79	.....	Williams.
"	Borneo manilla	141.4	176.7	138.24	.....	"
"	Singapore manilla	128.8	194.1	123.31	.....	"
"	Cleaned Sierra Leone	84.0	129.0	138.04	.....	"
"	Rough Sierra Leone	72.8	138.5	133.35	.....	"
"	Rough Accra	46.2	131.6	121.66	.....	"
"	Rough White Cengola	57.4	133.0	129.66	.....	"
"	Fine Clean Red Cengola	60.2	136.2	136.90	.....	"

Resin.	Variety.	Acid figure.	Koettstorfer figure.	Hübl figure.	Per cent. bromine absorbed.	Observer.
Copal	Unknown	57.4	122.2	142.24	.....	Williams.
"		....	123.9	.....	83.93	Mills.
"	Reduced to ⅔ by boiling,	....	128.9	.....	84.52	"
"	Boiled	114.4	....	.....	.....	"
"	Zanzibar	....	92.4	.....	.....	Schmidt and Erban.
"	"	....	89.6	.....	.....	" " "
"	" melted	0.0	36.8	.....	.....	" " "
"	" "	0.0	34.6	.....	.....	" " "
"	White Angola	....	132.2	.....	.....	" " "
"	" "	....	129.7	.....	.....	" " "
"	" " melted ..	93.6	118.8	44.9	.....	" " "
"	" " " ..	93.4	117.8	.....	.....	" " "
"	Red Angola.....	....	148.0	.....	.....	
	" "	....	146.4	.....	.....	
	" " melted	30.5	110.7	34.8	.....	
	" " "	30.0	109.8	.....	.....	
Dammar,	Batavia	22.4	36.4	117.67	.....	Williams.
"	Unknown	26.6	31.1	142.24	.....	"
"		....	52.3	.....	117.94	Mills.
"		33.0	47.1	63.6	.....	Schmidt and Erban.
		30.6	46.5	63.5	.....	" " "
Elemi		15.7	28.6	175.39	.....	Williams.
"		....	32.9	.....	122.23	Mills.
"		22.3	25.1	85.1	.....	Schmidt and Erban.
"		22.0	24.0	80.9	.....	" " "
Kauri	Medium.....	63.0	99.3	151.13	.....	Williams.
"	Fine	51.8	77.4	164.21	.....	"
"		....	128.8	.....	108.22	Mills.
Rosin.....	Refined	179.2	187.4	115.31	.....	Williams.
"	"	177.8	195.7	114.80	.....	"
"	Ordinary.....	169.4	176.4	112.02	.....	"
"	"	166.6	190.1	132.28	.....	"
"	Refined	....	181.0	.....	112.7	Mills.
"	Average of 5 samples ..	....	....	155.5	.....	McIlhiney.
"	Window glass	159.1	170.4	.....	.....	"
"	E.	168.5	189.9	.....	.....	"
"	A. Black.....	155.7	195.1	.....	.....	"
"		146.5	168.2	116.8	.....	Schmidt and Erban.
"		145.5	166.0	114.6	.....	" " "

The corresponding figures for linseed-oil are as follows:

Acidity should be 0.0. Mills allows one per cent. KOH for acidity.

Koettstorfer figure (Allen, *Commercial Organic Analysis*, **2**, 42). Nine samples, 187.4–195.2.

Hübl figure (Allen, *loc. cit.*, 50). Raw oil, 155–160; boiled oil, 148. Holde, *Mittheil. K. tech. Vers. Berlin, 1891*, **9**, 81, and *J. Soc. Chem. Ind.*, **12**, 179–180, 954.

Bromine absorption (Levallois, *J. pharm. chim.*, *1887*, **1**, 334), 100 per cent.

Mills (*J. Soc. Chem. Ind.*, **2**, 436). Raw oil, 76.09 per cent.; boiled oil, 102.36 per cent.

McArthur (*J. Soc. Chem. Ind.*, **7**, 64). Raw oil, 65.0–65.3 per cent.; boiled oil, 63.2–66.3 per cent.

The differences in solubility between linseed-oil and melted resins are but slight and are of little value in effecting separations in varnish analysis.

The Hübl figure is evidently useless as a means of quantitative analysis for the figures of linseed-oil and kauri the most frequently occurring resin, are almost identical.

The difference between the Koettstorfer figure is only about seventy-five, and even supposing that the figures of both oil and resin are known accurately, which is not the case, it would be difficult to make the analysis so carefully that the percentages of oil and resin would be correct.

Mills states that the analysis may be made by determining the acidity to phenolphthalein, and this proved to be correct, provided the mixture is composed of common rosin and linseed-oil and is not heated long. An analysis of such a mixture gave correct results but on attempting to apply the process to properly made varnishes the process was unsuccessful. Ten grams of a sample of varnish, known to contain 14.36 per cent. of kauri-resin, were diluted with a mixture of absolute alcohol, ether, and petroleum ether to obtain a clear solution, and then titrated with a solution of caustic soda in alcohol using phenolphthalein as indicator. The acidity found in this way was equal to only 0.345 per cent. of potassium hydroxide; this would mean an acidity of 2.40 per cent. for the kauri present, whereas Mills found 11.44 per cent., and Williams 6.3 per cent. Mills' statement that "it is evident that boiled oil when heated with a resin makes no difference in the resin's acidity," is not sustained by the facts.

The amount of bromine absorbed, as determined by the methods of Allen, Mills, and Levallois, is of no more use than the Hübl figure. The results depend largely upon the conditions under which the analysis is conducted.

In view of the fact that the bromine-addition figure of rosin is 0.0, while that of linseed-oil is 102, it seemed very likely that by means of this figure it would be possible to analyze varnish

residues. To test the process, a mixture was made of fifty per cent. common rosin and fifty per cent. oleic acid. The bromine-addition figure of the oleic acid used was 51.78 per cent., and that of the mixture 25.7 per cent., corresponding to 49.6 per cent. of oleic acid instead of fifty per cent. In order, if possible, to obtain samples of boiled oil and kauri-resin in the same condition in which they are present in varnishes, a quantity of boiled oil was heated in a retort to a temperature of 290° C. and maintained at this temperature for one hour. A sample of clear kauri-resin was also heated in a retort until it had lost twenty-three per cent. of its weight. The non-volatile part of a varnish of known composition was analyzed at the same time. The figures obtained were as follows:

Substance.	Bromine-addition figure.	Bromine-substitution figure.
Heated linseed-oil	76.62	4.82
Melted kauri-resin	21.53	80.31
Non-volatile of varnish C Kauri, 54.3 per cent., oil, 45.7 per cent.	89.16	22.84
Theoretical figures of above	46.71	45.81

The process therefore fails to give any means of making this analysis on account of changes made by the process of manufacture in the properties of oil and resin. It is well known to varnish-makers that treating together, effects remarkable changes in their physical properties, and that a certain amount of heating is necessary to make them knit together and work properly in the finished varnish.

Gladding (*Am. Chem. J.*, **3**, 416), has devised a process for determining common rosin in mixtures with fatty oils, depending upon the solubility of silver resinate in ether and the insolubility of silver oleate in the same medium. This process was tried on varnish but also failed to give satisfactory results. A varnish known to contain 14.36 per cent. of Kauri resin gave 25.9 per cent.

It is evident that the processes used in oil analysis are not adapted to the analysis of varnishes. The oil and resin react upon each other in some way not understood, giving rise to new compounds, and we must know something about what these compounds are, before the analytical problem can be solved.

THE ANALYSIS OF MALT.

By John A. Miller, Ph.D.

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HAVING been called upon during the past few years to assay a great many samples of malt I have been struck by the variation which existed between the results of my own analyses and those made by other chemists upon the same samples. The variations in some cases were too large to be placed within the possibility of experimental error. With the belief that these variations might, in part at least, be due to a greater or lesser degree of accuracy in the methods employed in the analysis of malt, I undertook a comparative investigation of three methods which are quite universally used.

From the stand-point of the brewer, the largest consumer of malt, what are the important points to be ascertained by the analysis of a malt sample?

1. Moisture.

2. Percentage of extract which the malt will yield when submitted to a miniature mashing process.

3. Diastatic power, that is the rapidity with which the starch contained in the malt is converted into sugar and dextrine.

4. The percentage of acidity (calculated as lactic acid) which the wort contains.

It has been claimed by some that the percentage of sugar formed and the amount of proteids dissolved is of importance in judging of the character of the malt. The amount of sugar is of no practical value to the brewer as the increase or decrease of the percentage of that article is entirely dependent upon the manner in which the malt is handled in the mash tub. The total nitrogen in the malt wort calculated as proteids is of little value since the percentage present in the finished beer will depend upon so many factors as to render the first results of comparatively little value. Amongst the factors which will influence this percentage are: Character of the water used in mashing; the use of a high or low initial mashing temperature; the length of time the wort is boiled in the kettle; the amount and character of the hops used; the character and quantity of yeast used; and the character of the fermentation.

The four points mentioned are of about equal importance in the assay of a malt sample.

The determination of moisture shows whether the malt has been properly dried and also whether the purchaser is not paying too high a price for an article which he can obtain very readily from the city water supply.

The determination of lactic acid is of value from the fact that it enables one to judge, within reasonable limits, of the age of the malt under examination. For example, a sample of malt which is low in moisture and high in lactic acid is an old malt which has been redried to bring down the high percentage of absorbed moisture.

In a first-class sample of malt the moisture should not run above five per cent., and the lactic acid 0.7 per cent.

Determination of Moisture.—Two methods were investigated in order to ascertain their relative accuracy. In the one method from two to four grams of ground malt was used; in the other twenty grams. In both cases the samples were heated to 100° C. until the weight was constant. Both methods gave results agreeing to within the third decimal place. The use of from two to four grams, however, is to be recommended:

1. Because it admits of the use of ground watch crystals for drying and weighing, thus preventing the absorption of moisture while the sample is cooling.

2. The time required to obtain a constant weight is much less than when twenty grams are used.

Determination of Extract.—The determination of the percentage of extract which a malt will yield is of very great importance, as upon this percentage, the value of the malt largely depends. It is evident that a sample of malt yielding fifty-five per cent. of extract has not the same commercial value as a malt yielding sixty per cent.

METHOD NO. I.

"Fifty grams of ground malt are weighed out as rapidly as possible (to avoid accession of water) and treated in a weighed beaker with 250 cc. of warm distilled water, of such a temperature that the initial heat of the mixture may be from 50°–52° C. The beaker containing the mash is placed in a water-bath and

the contents maintained at the same temperature for a quarter of an hour. The heat is then gradually raised till the immersed thermometer registers 59°–60° C., and the temperature is then kept constant till a drop taken from the liquid ceases to give a blue color with iodine solution and nearly ceased to give a brown. This shows that all the starch and nearly all the erythrodextrine has suffered hydrolysis—a point which will be reached in about twenty minutes. The heat is then increased to about 70° C. in order to complete the saccharification, when the water in the bath is boiled for five minutes. This step which completes the process of mashing should be arrived at in about 100 minutes from the commencement of the operation. The beaker is then cooled and the contents filtered. The insoluble matter is washed with cold water and the filtrate is made up exactly to 400 cc. The density of the clear wort is next taken at 15.5° C. in the usual way by a specific gravity bottle. The excess of density over that of water (taken as 1,000) multiplied by 2.078 will give the percentage of dry extract yield by the malt. Instead of ascertaining the gravity of the infusion, the proportion of solid matter may be determined by evaporating a known measure of the wort to dryness in a flat-bottomed dish, so that the residue may form a thin film. The extract dried at 105° C. till constant in weight."

Two portions of fifty grams each of the same sample of malt treated as indicated above gave the following results:

	I.	II.
Specific gravity of the wort	1.0284	1.0284
Extract calculated by factor	59.01 per cent.	59.01 per cent.

5.142 grams of the wort were then taken and placed in a wide flat-bottomed platinum dish and the extract dried at 105° C. to almost constant weight. The following was obtained:

	I.	II.
Weight of the extract	0.3496 gram.	0.3488 gram.
Average weight	0.3492 gram.	
Percentage of extract	55.87	

5.142 grams were again taken and placed in a flat-bottomed dish and this in a water oven, the temperature of which was kept at 70°–75° C., and the extract dried to constant weight. The time required for this was about seventy hours.

	I.	II.
Weight of the extract	0.3694 gram.	0.3681 gram.
Average weight	0.3687 gram.	
Percentage of extract	58.992	

METHOD NO. II.

"Fifty grams of ground malt are carefully weighed as rapidly as possible. The ground malt is put into a copper beaker, the weight of which is known, and this beaker is placed in a water-bath. Water is now mixed with the malt to the amount of 200 cc., at a temperature of 38° R. This temperature is held while the malt is continuously stirred for thirty minutes, when the temperature is raised to 58° R., 4° R. each five minutes. When the temperature of 58° R. is reached tests are made in order to find out whether the starch has been converted completely. Usually we find that after the temperature of 58° R. has been reached all the starch is converted. The mash is always held thirty minutes after the temperature of 58° R. has been reached, when it is boiled for five minutes, cooled off, and water enough is added to make the weight of the contents of the beaker, or the weight of the entire mash, 350 grams. The wort is then filtered off. After the wort has been filtered the specific gravity is taken from which the per cent. Balling is ascertained and the amount of extract in the malt computed to the following formula; *viz.*,"

$$\frac{(600 + \text{per cent. water}) \times \text{per cent. Balling}}{100 - \text{per cent. Balling.}}$$

Two mashes of fifty grams of malt gave the following:

	I.	II.
Specific gravity of the wort	1.0385	1.0383
Average specific gravity	1.0384	
Extract calculated by formula	63.85 per cent.	
Moisture in the malt	7.53 "	"

5.192 grams of wort was then placed in a flat-bottomed dish and dried at 105° C. to almost constant weight. Results; *viz.*,

	I.	II.
Weight of extract	0.4520 gram.	0.4522 gram.
Average weight	0.4521 gram.	
Extract	54.25 per cent.	

The same amount of wort dried at 70°–75° C. for about seventy hours gave:

	I.	II.
Weight of extract	0.4924	0.4922
Average weight	0.4923 gram.	
Extract	59.07 per cent.	

METHOD NO. III.

Fifty grams of ground malt are weighed out as rapidly as possible, then placed in a weighed copper beaker and mixed with 200 cc. of water of a temperature of 40° C. The whole mixture is then carefully heated on an asbestos plate until the immersed thermometer registers 60° C. This temperature of 60° C. is maintained for twenty minutes, the mixture being almost constantly stirred during this time. At the end of twenty minutes a few drops of the solution are tested with iodine solution in order to ascertain whether the saccharification is complete. If the iodine gives the starch or erythrodextrine reaction the mash is further heated, the temperature being carefully raised 1° every two minutes until iodine solution ceases to give any reaction. It is very seldom that the temperature will go above 70° C. The flame is then removed, the mash cooled down and enough water added to make the total amount used equal to 400 grams, or the weight of the mash, that is, the malt plus the water equal 450 grams. After thoroughly mixing, the mash is thrown upon a plaited filter. The first half of the wort which filters through is thrown back upon the filter and then all which filters through collected. The specific gravity of this filtrate, or wort, is then taken by means of the Westphal balance. From this gravity the percentage given by Schultze's tables is ascertained and that number multiplied by 8.75, which gives the percentage of dry extract yield from the malt. The percentage can also be calculated by the use of the following formula:

$$\frac{(800 - \text{per cent. water}) \times \text{per cent. Schultze}}{100 - \text{per cent. Schultze.}}$$

The Schultze tables are so arranged that they give the amount of extract in 100 grams of wort of the specific gravity obtained. It would be a natural conclusion that the percentage represented by Schultze tables should be multiplied by 8 in order to obtain the amount of extract in 100 grams of malt, but this factor gives results which are below the absolute amount of extract which may be obtained from the malt. As the result of actual

brewing experience I am of the opinion that the percentage Schultze multiplied by the factor 8 represents the amount of extract which the average brewer obtains from his material in actual practice, although the absolute amount obtainable on a small scale is higher. Two mashes of fifty grams each gave:

	I.	II.
Specific gravity of wort	1.0285	1.0285
Extract calculated from Schultze's table. Factor 8	58.96 per cent.	58.96 per cent.
Factor 8.75	64.487 " "	64.487 " "
Extract calculated by formula	64.24 " "	64.24 " "

5.1425 grams of this wort were placed in a flat-bottomed dish and dried at 105° C. to almost constant weight. Results; *viz.*,

	I.	II.
Weight of extract	0.3511 gram.	0.3494 gram.
Average weight of extract	0.3502 gram.	
Extract	56.03 per cent.	

The same amount dried at 70°–75° C. for about seventy hours to constant weight gave:

	I.	II.
Weight of extract	0.3700 gram.	0.3681 gram.
Average weight	0.3690 gram.	
Extract	59.04 per cent.	

In order to ascertain what variation, if any, existed between these results and the absolute amount of extract obtainable I made another mash from the same sample of malt which had been used for the preceding experiments. Method No. III was used with this exception that it was not made up to 400 grams, but was at once thrown upon a filter and washed with water at a temperature of 58° C. until the filtrate gave no reaction for sugar with Fehling's solution. This filtrate was then made up to 1,000 cc. and an aliquot part dried at 70°–75° C. to constant weight. Two portions of ten cc. each gave:

	I.	II.
Extract by weight in ten cc.	0.3237 gram.	0.3236 gram.
" in 1,000 cc.	32.37 "	32.36 "
Percentage of extract from malt,	64.74	64.72
Average percentage	64.73.	

The variations existing between the results obtained is apparent in the following table:

	METHODS.		
	No. I.	No. II.	No. III.
Per cent. of extract calculated according to the directions of the method,	59.01	63.85	64.487
Method III using factor 8	....	....	58.96
" " " formula	....	....	64.24
Extract dried at 105° C.	55.87	54.25	56.03
" " " 70°–75° C.	58.99	59.07	59.04
Absolute per cent. of extract obtainable,	....	....	64.73

A comparison of these results show that methods II and III give us figures agreeing closer to the actual amount of extract obtainable from the malt than method No. I, but even these are a little below the actual content. No. III, however, only slightly so. The results obtained by drying at 105° C. are too low and untrustworthy owing to a decomposition during the process of drying, as will be shown later in this paper. Looking at the results of the three methods as obtained by drying the extract at 70°–75° we find an excellent agreement between the maximum and minimum results, but a wide variation from the absolute amount of extract. This would indicate that a marked amount of starch was not saccharified and consequently would be lost as extract. It was only obtained by the washing of the grains with warm water.

Extract dried at 105° C.—In order to ascertain why the extract dried at 105° C. was so much lower than when calculated or dried at 70°–75°, a malt analysis was made with the following results:

	Method III.
Calculated per cent. of extract using factor 8,	58.40 per cent.
Extract dried at 70°–75°	58.25 " "
" " " 105°	54.01 " "

The percentage of extract obtained by drying at 105° is over four per cent. lower than the percentage of extract obtained by the other methods. This would indicate that either the percentage of extract was actually lower than indicated by the other methods of determination, or that some substance had undergone decomposition and occasioned a loss which reduced the percentage. I was of the belief that the maltose had suffered decomposition at the temperature of 105° and therefore lowered the percentage of extract.

Determinations of sugar were consequently made:

1. In the wort obtained by method III and calculated to the total amount of extract obtained.

2. The maltose or sugar contained in the extract dried at 70°–75° was determined and a calculation made for the total from these results.

3. The sugar contained in the extract dried at 105° was determined and a similar calculation made.

	Maltose.
Method No. III	37.50 per cent.
Extract dried at 70°–75°	37.50 " "
" " " 105°	31.50 " "

It will be seen that the percentage of maltose obtained from the extract dried at 105° is six per cent. lower than that obtained from the original wort and from the extract dried at 70°–75°. This rather clearly indicates that a decomposition of maltose has taken place with a consequent loss.

In every case the extract dried at 105° was almost black in appearance and had a distinct burnt sugar odor.

CONCLUSIONS.

1. Methods II and III give results almost equal in accuracy. No. III giving nearer the absolute amount of extract obtainable when the factor 8.75 is used. It is furthermore a preferable method as it requires less time for the analysis than No. II. And where a number of samples are handled, time is an important item.

2. Method I is inaccurate as the results obtained are much below the actual amount of extract.

3. The extract can not be determined by drying at 105° owing to the decomposition of the maltose at that temperature. This applies to the determination of extract in beer as well as in unfermented worts.

4. The washing of the grains until no sugar reaction is obtained and the subsequent drying of the extract at 70°–75° C. is impracticable, except for scientific purposes, as the amount of time required for the completion of an analysis is too great.

I would recommend method III as the simplest; it is accurate when the factor 8.75 is used, and requires the least time. It is the method upon which a subsequent paper on diastatic power will be based.

I wish, here, to express my sincere thanks to my assistant, Mr. W. I. Tibbals, for the very able and enthusiastic manner in which he has assisted me in this investigation.

NIAGARA UNIVERSITY, BUFFALO, N. Y.